



DECLARATION

I, Kinshiro TSUKUDA, a national of Japan, c/o Sumitomo Chemical Intellectual Property Service, Limited, 5-33, Kitahama 4-chome, Chuo-ku, Osaka-shi, Osaka 541-8550, Japan, declare that to the best of my knowledge and belief the attached is a full, true and faithful translation into English made by me of the certified copy of Japanese Patent Application No. 2002-319504 attached thereto.

Signed this 17th day of January, 2005

A handwritten signature in cursive script, appearing to read "Kinshiro Tsukuda", written over a horizontal line.

Kinshiro TSUKUDA



JAPANESE PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Application Number : Japanese Patent Application
No. 2002-319504
Applicant(s) : SUMITOMO CHEMICAL COMPANY, LIMITED

30 May, 2003

Commissioner,
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Patent Application No. 2002-319504

[Name of Document] Correction Data
[Document Corrected] Patent Application

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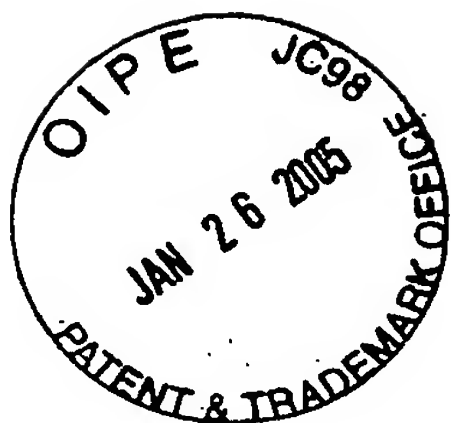
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Patent Application No. 2002-319504

Applicant's Past Record

Applicant's ID Number [000002093]

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[Reason for Alteration] New Registration

Address 5-33, Kitahama 4-chome, Chuo-ku, Osaka-shi,
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[Priority Claiming Based on the Prior Application]

[Application Number] No. 2002-244971
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[List of Articles Filed]

[Name of Article] Specification 1
[Name of Article] Abstract 1
[Number of General Power] 0212949

[Necessity of Proof] Necessary



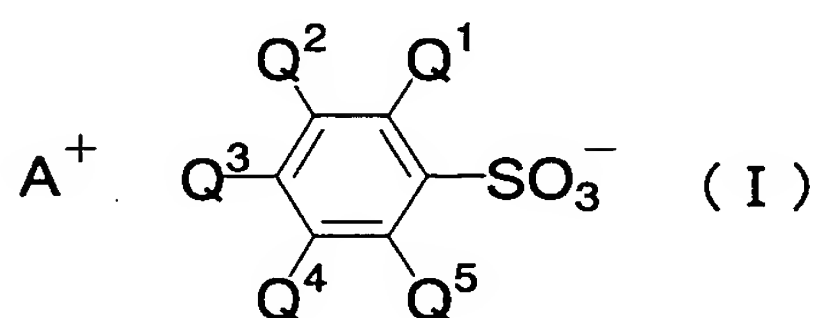
[DOCUMENT NAME] Specification

[TITLE OF THE INVENTION] ACID GENERATOR AND RESIST COMPOSITION

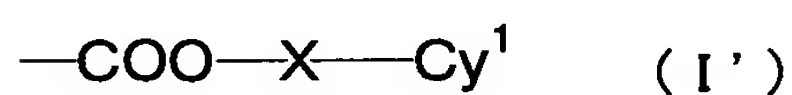
[SCOPE OF CLAIMS]

5 [Claim 1]

A salt of the formula (I):



wherein Q^1 , Q^2 , Q^3 , Q^4 and Q^5 each independently represent hydrogen,
optionally branched alkyl having 1 to 16 carbon atoms, optionally branched
10 alkoxy having 1 to 16 carbon atoms, halogen, aryl having 6 to 12 carbon atoms,
aralkyl having 7 to 12 carbon atoms, cyano, sulfide, hydroxy, nitro or a group of
the formula (I')



wherein X represents alkylene or alklene optionally containing thioether bond or
15 ether bond, and Cy^1 represents alicyclic hydrocarbon group having 3 to 20
carbon atoms,

and A^{+} represents a counter ion, with the proviso that at least one of Q^1 , Q^2 , Q^3 ,
 Q^4 and Q^5 is the group of the formula (I').

[Claim 2]

20 The salt according to Claim 1, wherein X in the formula (I') is alkylene.

[Claim 3]

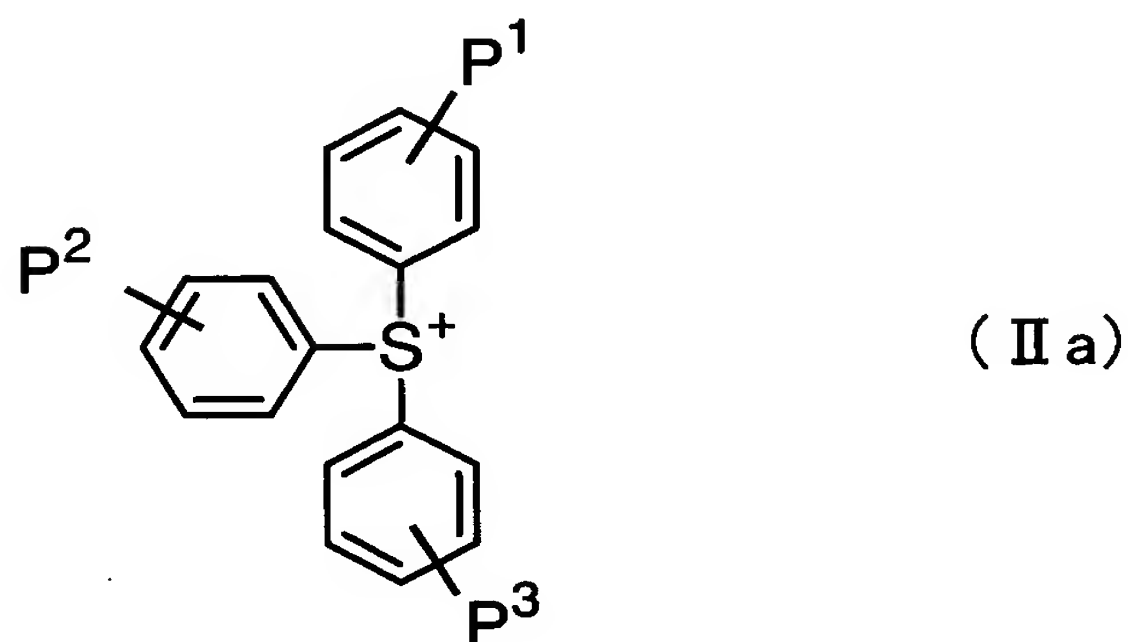
The salt according to Claim 1 or 2, wherein Cy^1 in the formula (I') is

cyclohexyl, 2-norbornyl, 1-adamantyl or 2-adamantyl.

[Claim 4]

The salt according to any of Claims 1 to 3, wherein A^+ is the formula

(IIa)

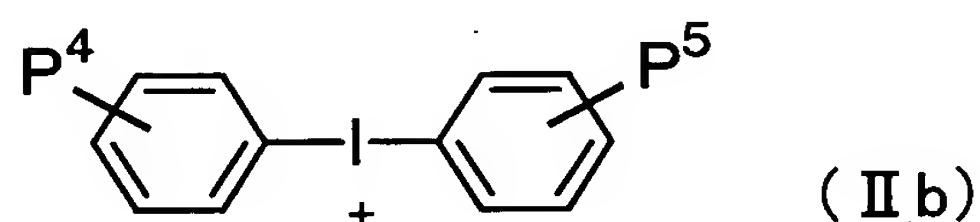


wherein P^1 , P^2 and P^3 each independently represent hydrogen, hydroxyl, alkyl having 1 to 6 carbon atoms or alkoxy having 1 to 6 carbon atoms.

[Claim 5]

The salt according to any of Claims 1 to 3, wherein A^+ is the formula

10 (IIb)



wherein P^4 and P^5 each independently represent hydrogen, hydroxyl, alkyl having 1 to 6 carbon atoms or alkoxy having 1 to 6 carbon atoms.

[Claim 6]

15 The salt according to any of Claims 1 to 3, wherein A^+ is the formula

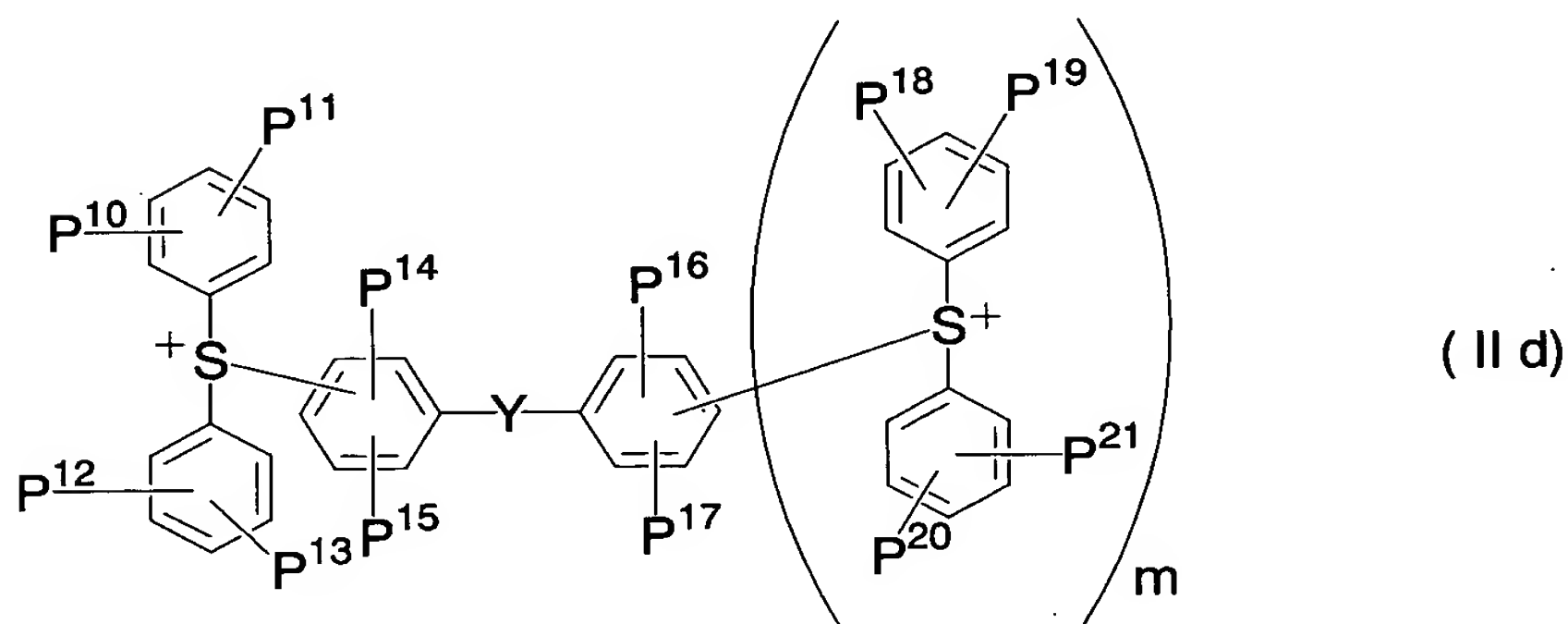
(IIc)



wherein P^6 and P^7 each independently represent alkyl having 1 to 6 carbon atoms or cycloalkyl having 3 to 10 carbon atoms, or P^6 and P^7 bond to form alicyclic hydrocarbon group having 3 to 7 carbon atoms, said alicyclic hydrocarbon group may have ketone group, and at least one $-\text{CH}_2-$ in the alicyclic hydrocarbon group may be substituted by oxygen or sulfur; P^8 represents hydrogen, P^9 represents alkyl having 1 to 6 carbon atoms, cycloalkyl having 3 to 10 carbon atoms or aromatic ring group optionally substituted, or P^8 and P^9 bond to form alicyclic hydrocarbon group.

10 [Claim 7]

The salt according to any of Claims 1 to 3, wherein A^+ is the formula (II d)



wherein P^{10} to P^{21} each independently represent hydrogen, hydroxyl, alkyl having 1 to 6 carbon atoms or alkoxy having 1 to 6 carbon atoms, Y represents sulfur or oxygen, and m represents 0 or 1.

[Claim 8]

A chemical amplification type positive resist composition comprising resin which has a structural unit having an acid labile group and which itself is insoluble or poorly soluble in an alkali aqueous solution but becomes soluble in an alkali aqueous solution by the action of an acid, and a salt described in any of
 5 Claims 1 to 7.

[Claim 9]

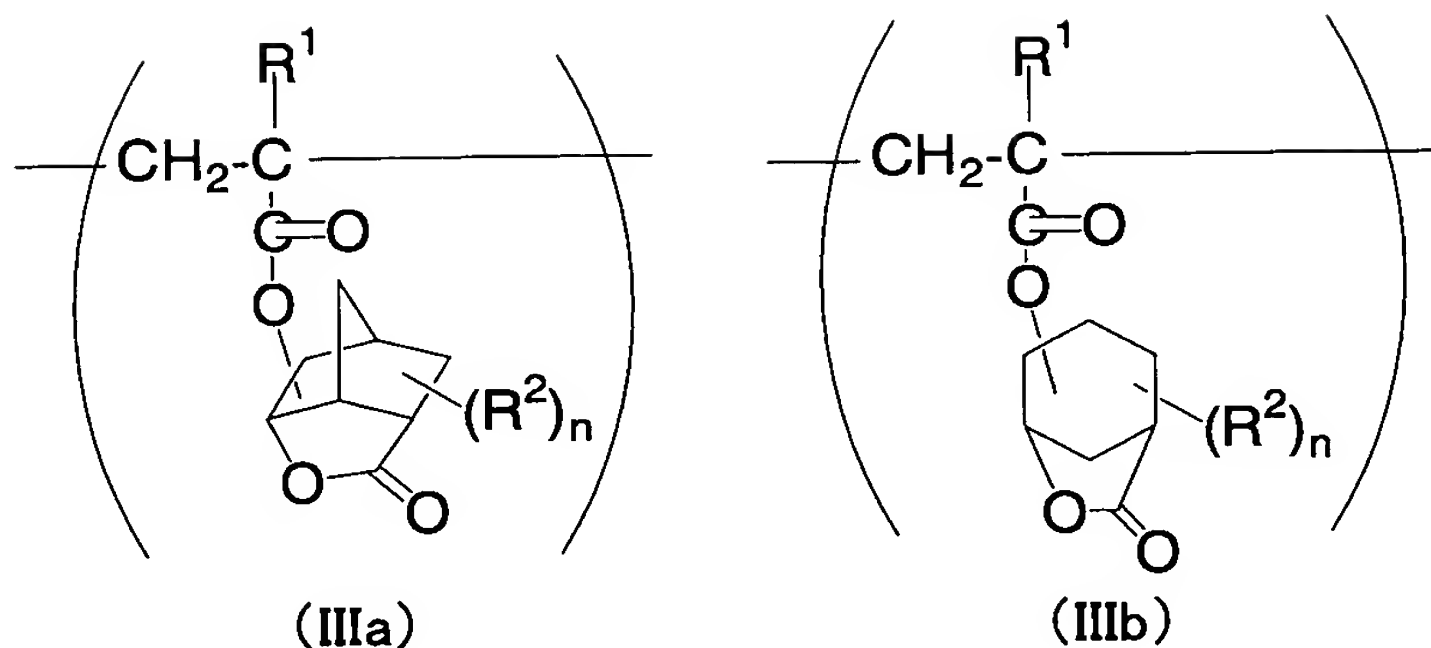
The composition according to Claim 8 wherein the content of the structural unit having an acid-labile group in all structural units of the resin is from 10 to 80%.

10 [Claim 10]

The composition according to Claim 8 or 9 wherein the structural unit having an acid-labile group is a structural unit derived from 2-alkyl-2-adamantyl (meth)acrylate or 1-(1-adamantyl)-1-alkylalkyl (meth)acrylate.

[Claim 11]

15 The composition according to any of Claims 8 to 10 wherein the resin contains, in addition to the structural unit having an acid-labile group, further at least one structural unit selected from the group consisting of a structural unit derived from p-hydroxystyrene, a structural unit derived from m-hydroxystyrene, a structural unit derived from 3-hydroxy-1-adamantyl
 20 (meth)acrylate, a structural unit derived from 3,5-dihydroxy-1-adamantyl (meth)acrylate, a structural unit derived from (meth)acryloyloxy- γ -butyrolactone having a lactone ring optionally substituted by alkyl, a structural unit of the formula (IIIa) and a structural unit of the following formula (IIIb)



wherein R^1 and R^2 each independently represent hydrogen, methyl, trifluoromethyl or halogen, and n represents an integer of 1 to 3.

[Claim 12]

5 The composition according to any of Claims 9 to 11 wherein the resin further contains a structural unit derived from 2-norbornene and a structural unit derived from an aliphatic unsaturated dicarboxylic anhydride.

[Claim 13]

10 The composition according to any of Claims 8 to 12 wherein the composition further comprises amine as a quencher.

[Claim 14]

 The composition according to any of Claims 8 to 13 wherein the composition further comprises a surfactant.

[DETAILED DESCRIPTION OF THE INVENTION]

15 [0001]

[Technical Field Pertinent to the Invention]

 The present invention relates to a novel salt used in fine processing of semiconductors and resist composition containing the salt.

[0002]

[Prior Art]

Semiconductor microfabrication employs a lithography process using a resist composition. In lithography, theoretically, the shorter the exposure wavelength becomes, the higher the resolution can be made, as expressed by

5 Rayleigh's diffraction limit formula. The wavelength of an exposure light source for lithography used in the manufacture of semiconductor devices has been shortened year by year as g line having a wavelength of 436 nm, i line having a wavelength of 365 nm, KrF excimer laser having a wavelength of 248 nm and ArF excimer laser having a wavelength of 193 nm. F₂ excimer laser

10 having a wavelength of 157 nm seems to be promising as the next-generation exposure light source. Further, as the exposure light source of the subsequent generation, soft X ray (EUV) having a wavelength of 13 nm or shorter has been proposed as the exposure light source following the 157nm-wavelength F₂ excimer laser.

15 [0003]

Since light sources having shorter wavelength than that of g line and i line, such as excimer laser and the like have low illumination, it is necessary to enhance the sensitivity of a resist. Consequently, there are used so-called chemical amplification type resists utilizing the catalytic action of an acid

20 produced from a sulfonium salt, iodonium salt, and the like by exposure and containing a resin having a group being dissociated by this acid.

[0004]

However, in conventionally known chemical amplification type resist compositions, there is a problem that line edge roughness occurs by generation

of standing wave and the like, namely, smoothness on a pattern side wall decreases, and resultantly, uniformity of line width deteriorates.

Though it is known that the use of an acid generator including anion of benzenesulfonic acid having at least one ester group in a positive type
5 photosensitive composition (for example, Patent Document 1), it is still difficult to combine progress of roughness and progress of pattern shapes.

[0005]

[Patent Document 1]

JP-H09-244234-A (Pages 1 to 4)

10 [0006]

[Problems to be solved by the Invention]

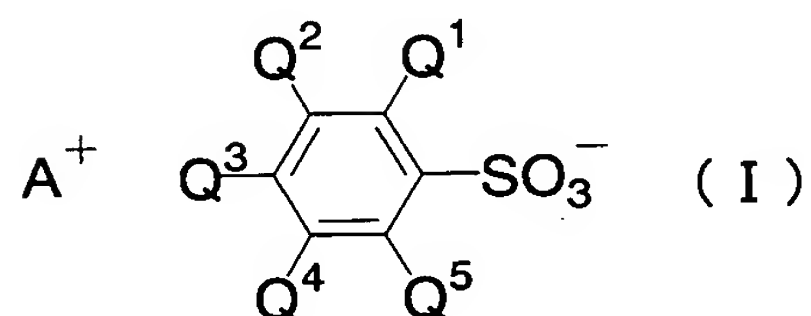
An object of the present invention is to provide a novel salt used for chemical amplification type resist and to provide a chemical amplification type resist composition comprising the above-mentioned salt and a resin component,
15 and suitable for excimer laser lithography using ArF, KrF, and the like, showing excellent various resist abilities such as sensitivity, resolution and the like, and giving particularly improved line edge roughness and pattern profiles.

[0007]

The present inventors have conducted extensive studies, and as a result,
20 has found that a chemical amplification type positive resist composition using a specific benzenesulfonate anion derivative provides patterns showing excellent various resist abilities such as sensitivity, resolution and the like, and giving particularly improved line edge roughness and pattern profiles, and thus the present invention was completed.

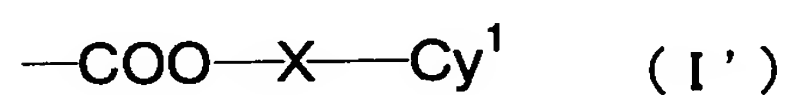
That is, the present invention relates to

<1>alt of the following formula (I):



wherein Q^1 , Q^2 , Q^3 , Q^4 and Q^5 each independently represent hydrogen,

- 5 optionally branched alkyl having 1 to 16 carbon atoms, optionally branched alkoxy having 1 to 16 carbon atoms, halogen, aryl having 6 to 12 carbon atoms, aralkyl having 7 to 12 carbon atoms, cyano, sulfide, hydroxy, nitro or a group of the formula (I')



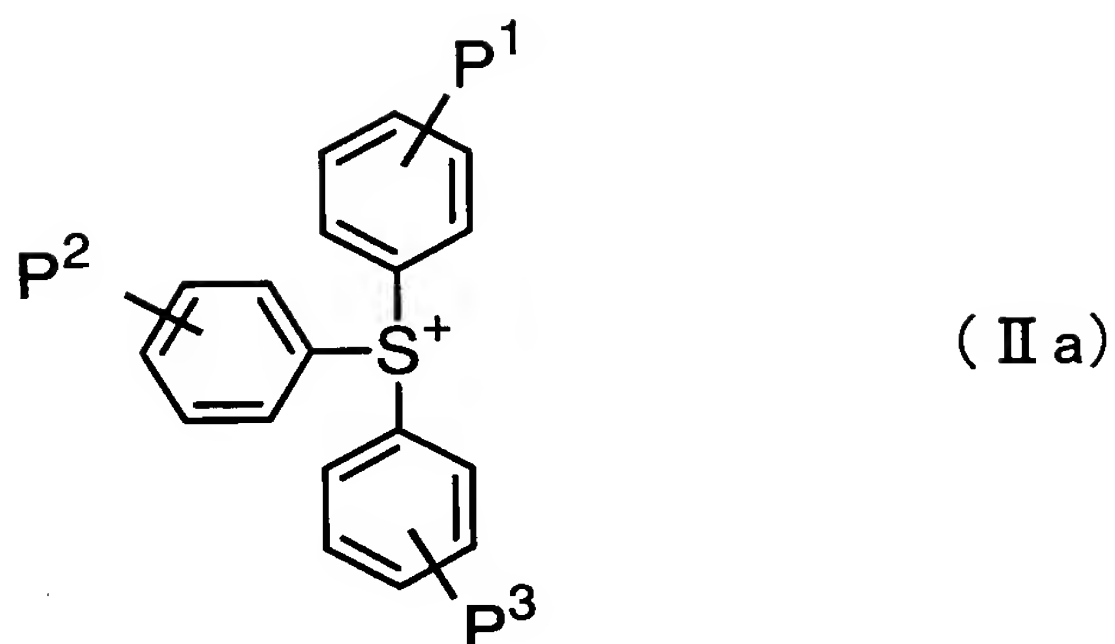
- 10 wherein X represents alkylene or alklene optionally containing thioether bond or ether bond, and Cy^1 represents alicyclic hydrocarbon group having 3 to 20 carbon atoms,

and A^+ represents a counter ion, with the proviso that at least one of Q^1 , Q^2 , Q^3 , Q^4 and Q^5 is the group of the formula (I').

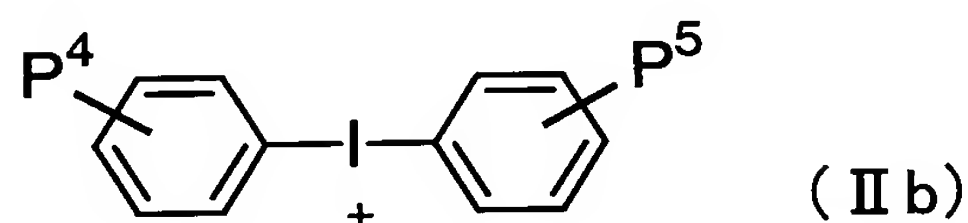
15 [0008]

The present invention also relates to

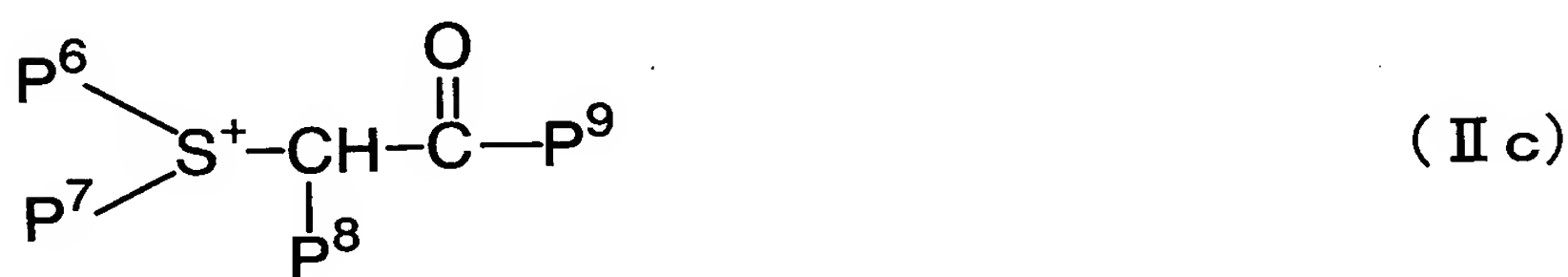
<2> a salt wherein, in the formula (I), A^+ is the formula (IIa), (IIb), (IIc) or (IIc):



wherein P^1 , P^2 and P^3 each independently represent hydrogen, hydroxyl, alkyl having 1 to 6 carbon atoms or alkoxy having 1 to 6 carbon atoms;



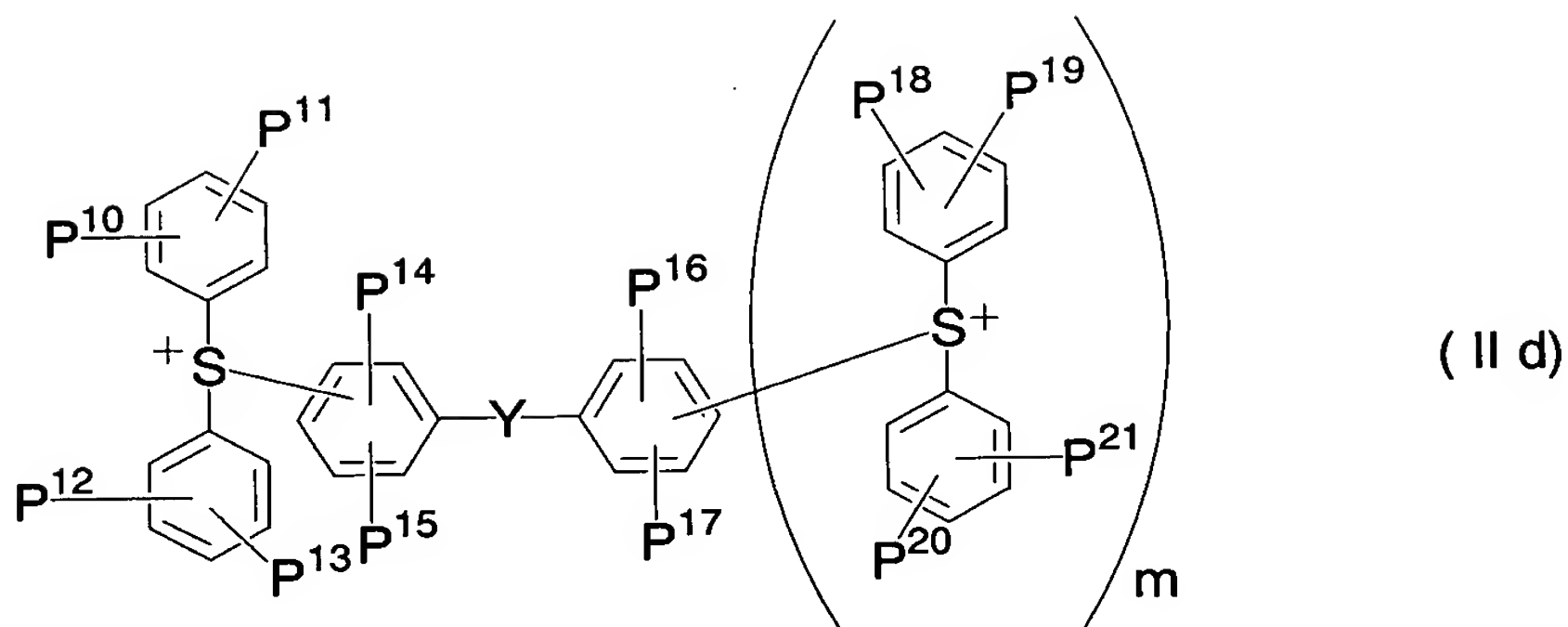
5 wherein P^4 and P^5 each independently represent hydrogen, hydroxyl, alkyl having 1 to 6 carbon atoms or alkoxy having 1 to 6 carbon atoms;



wherein P^6 and P^7 each independently represent alkyl having 1 to 6 carbon atoms or cycloalkyl having 3 to 10 carbon atoms, or P^6 and P^7 bond to form alicyclic hydrocarbon group having 3 to 7 carbon atoms, said alicyclic hydrocarbon group may have ketone group, and at least one $-CH_2-$ in the alicyclic hydrocarbon group may be substituted by oxygen or sulfur; P^8 represents hydrogen, P^9 represents alkyl having 1 to 6 carbon atoms, cycloalkyl having 3 to 10 carbon atoms or aromatic ring group optionally substituted, or P^8 and P^9 bond to form alicyclic hydrocarbon group;

10

15



wherein P^{10} to P^{21} each independently represent hydrogen, hydroxyl, alkyl having 1 to 6 carbon atoms or alkoxy having 1 to 6 carbon atoms, Y represents sulfur or oxygen, and m represents 0 or 1.

5 [0009]

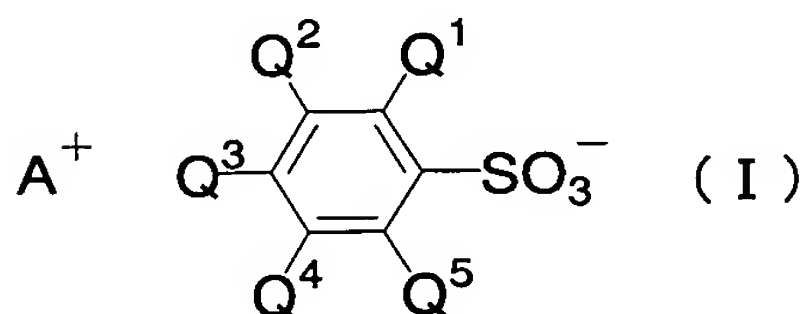
The present invention further relates to

<3> a chemical amplification type positive resist composition comprising resin which has a structural unit having an acid labile group and which itself is insoluble or poorly soluble in an alkali aqueous solution but becomes soluble in
 10 an alkali aqueous solution by the action of an acid, and a salt described in <1> or <2> above.

[0010]

[Mode for carrying out the Invention]

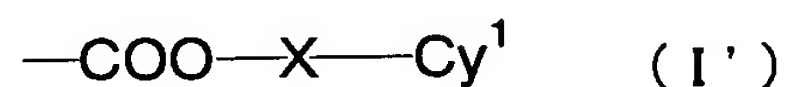
The present salt is represented by the following formula (I):



15

wherein Q^1 , Q^2 , Q^3 , Q^4 and Q^5 each independently represent hydrogen, optionally branched alkyl having 1 to 16 carbon atoms, optionally branched

alkoxy having 1 to 16 carbon atoms, halogen, aryl having 6 to 12 carbon atoms, aralkyl having 7 to 12 carbon atoms, cyano, sulfide, hydroxy, nitro or a group of the formula (I')



5 wherein X represents alkylene or alkene optionally containing thioether bond or ether bond, and Cy^1 represents alicyclic hydrocarbon group having 3 to 20 carbon atoms,

and A^+ represents a counter ion, with the proviso that at least one of Q^1 , Q^2 , Q^3 , Q^4 and Q^5 is the group of the formula (I').

10 Examples of the optionally branched alkyl having 1 to 16 carbon atoms include methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, pentyl, hexyl, octyl, decyl, dodecyl, hexadecyl, and the like.

Examples of the optionally branched alkoxy having 1 to 16 carbon atoms include methoxy, ethoxy, propoxy, isopropoxy, butoxy, tert-butoxy, pentyloxy, 15 hexyloxy, isopentyloxy, decyloxy, dodecyloxy, hexadecyloxy, and the like.

Examples of halogen include fluorine, chlorine, bromine and iodine.

Examples of aryl having 6 to 12 carbon atoms include phenyl, tolyl, methoxyphenyl, naphthyl and the like.

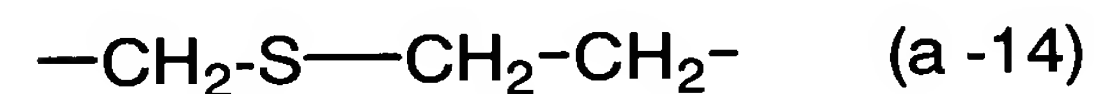
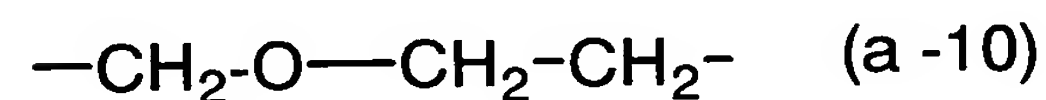
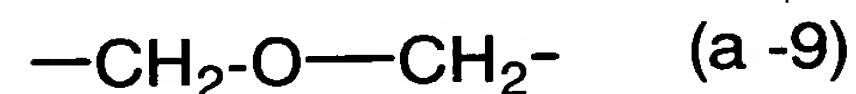
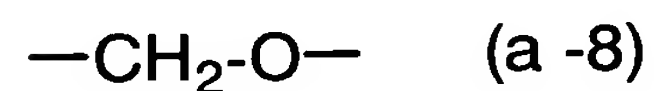
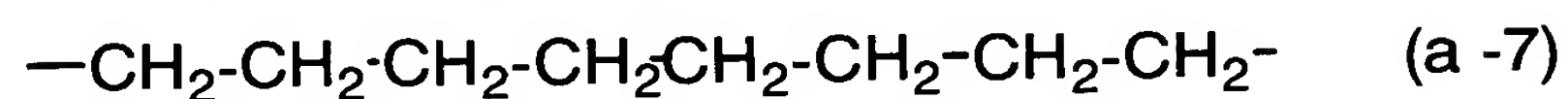
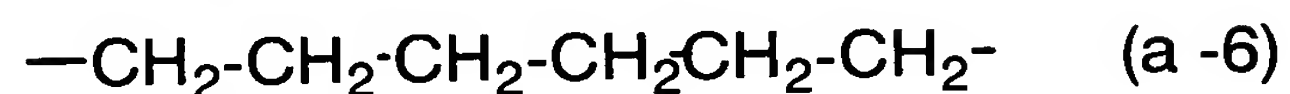
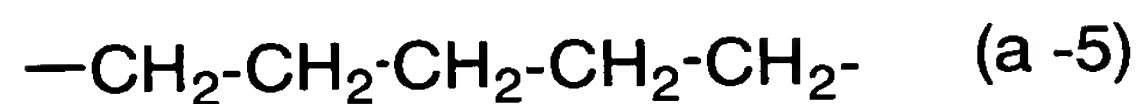
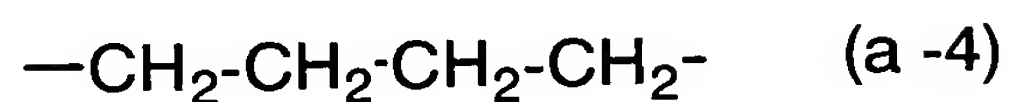
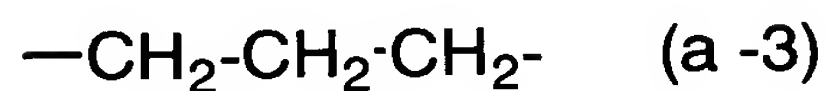
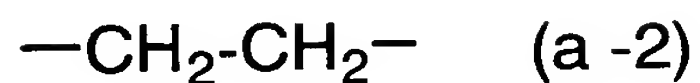
Examples of the aralkyl having 7 to 12 carbon atoms include benzyl, 20 chlorobenzyl, methoxybenzyl, and the like.

[0011]

When two or more of Q^1 , Q^2 , Q^3 , Q^4 and Q^5 are the groups of the formula (I'), the groups of the formula (I') may independently be selected.

[0012]

Examples of X include the followings:

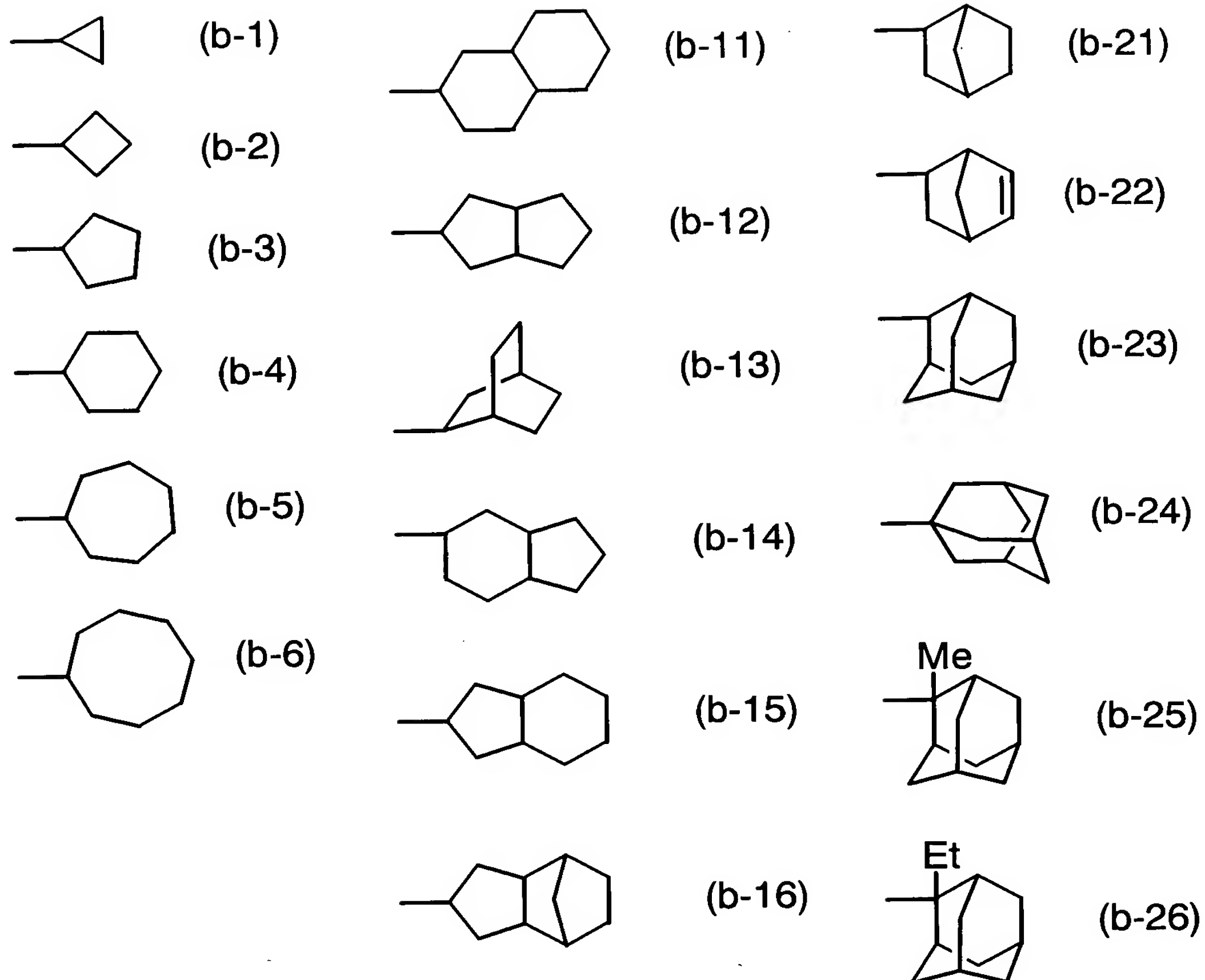


In the formulae above, alkylenes of (a-1) to (a-7) are preferred.

[0013]

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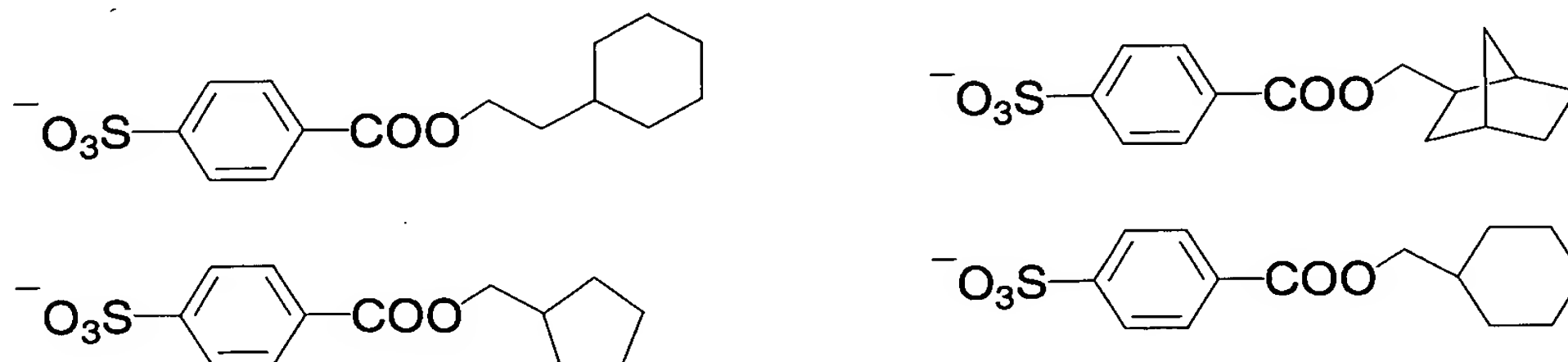
Examples of Cy^1 include the followings:

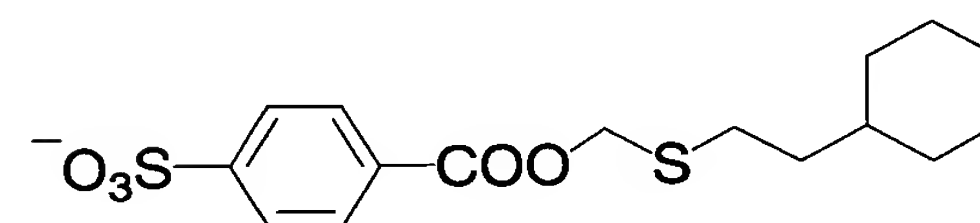
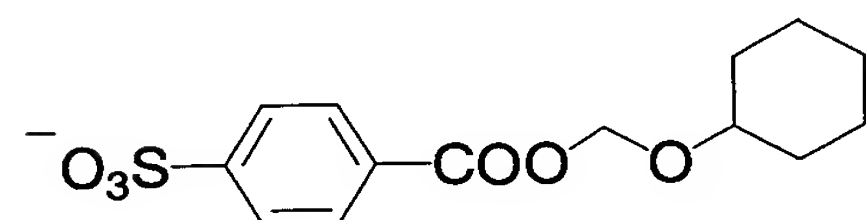
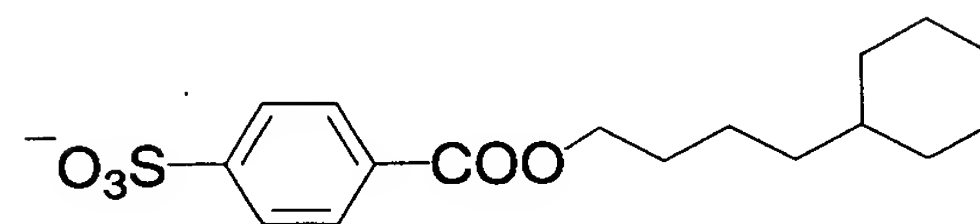
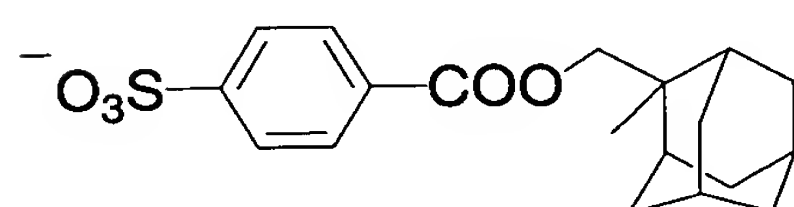
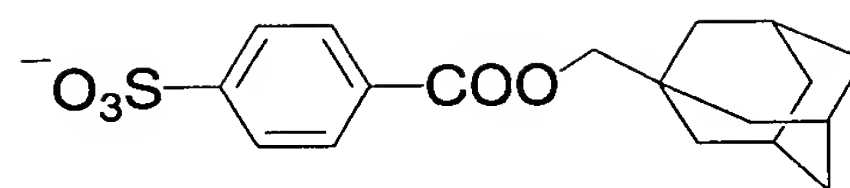
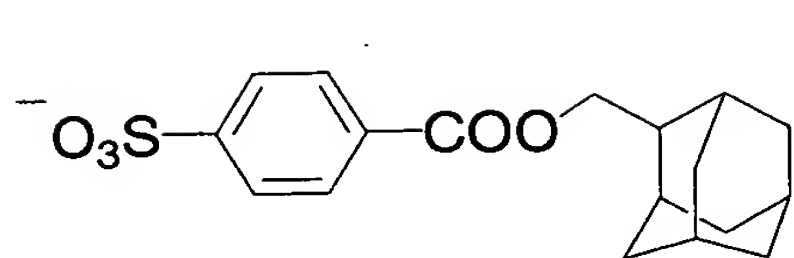


In the formulae above, cyclohexyl (b-4), 2-norbornyl (b-21), 1-adamantyl (b-24) and 2-adamantyl (b-23) are preferred.

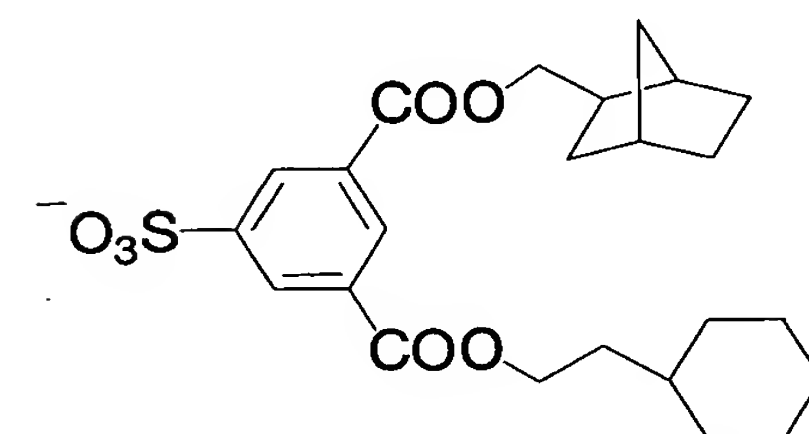
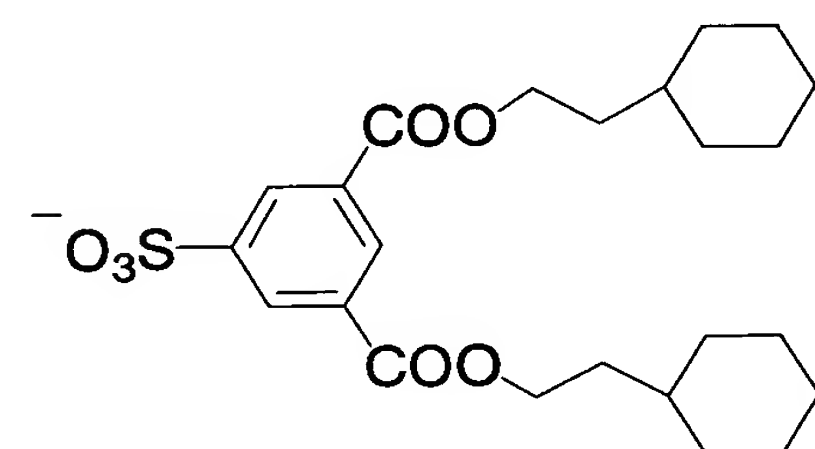
[0014]

5 Specific examples of the anion part in the salt of the formula (I) include the followings:

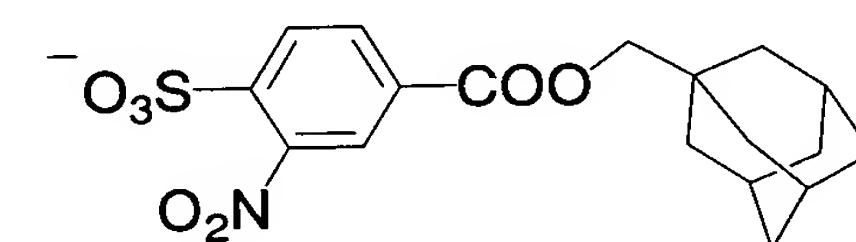
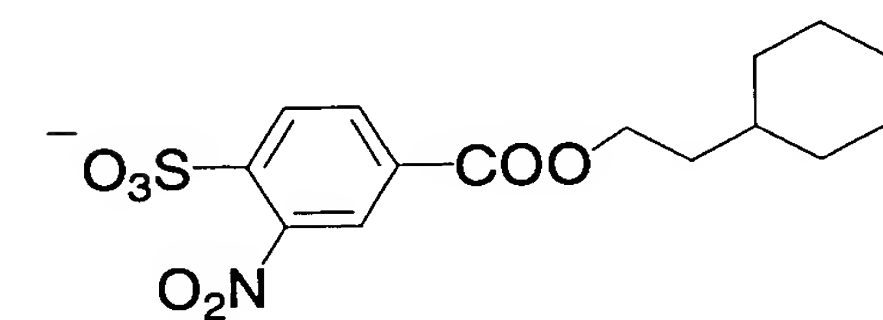
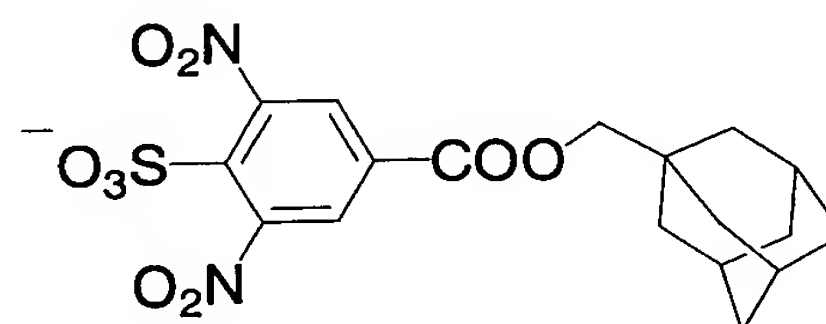
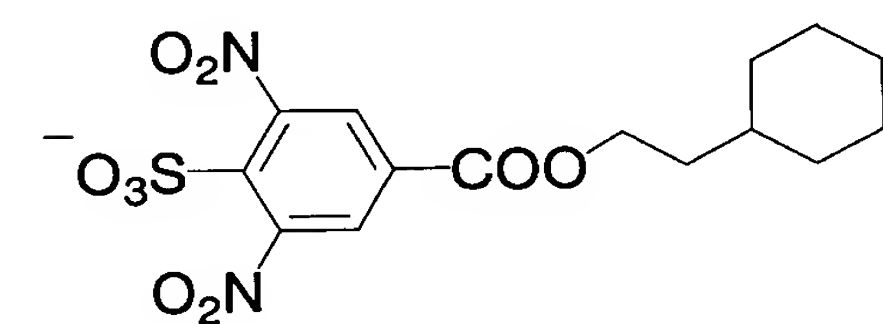
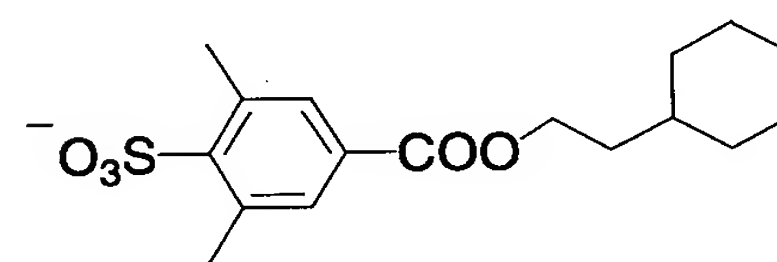
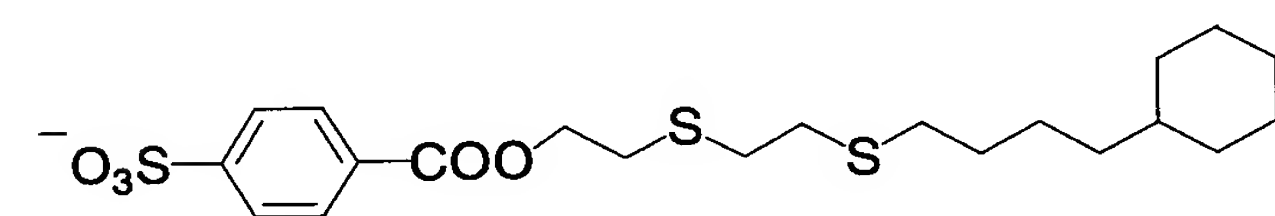
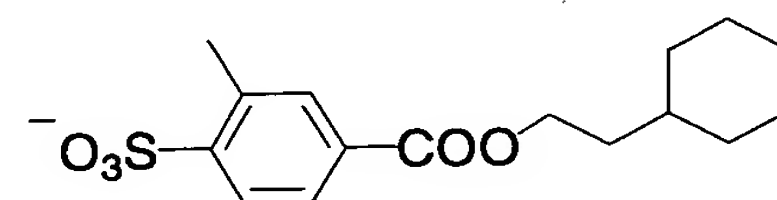
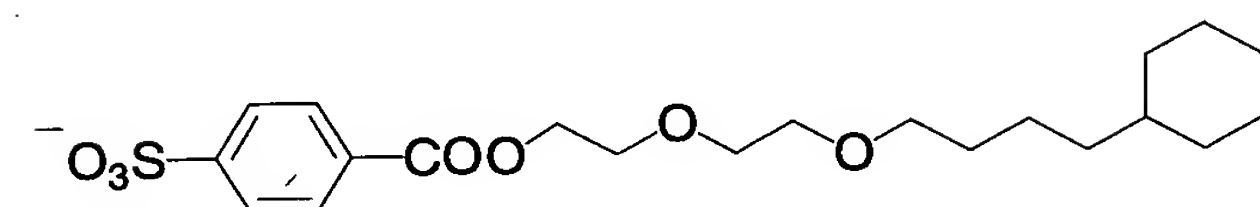




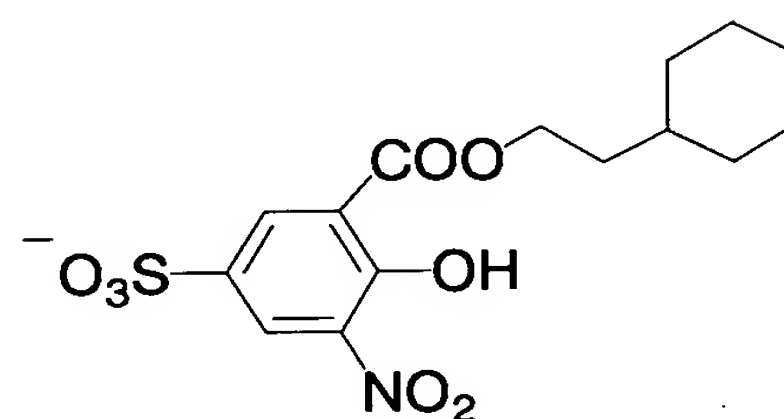
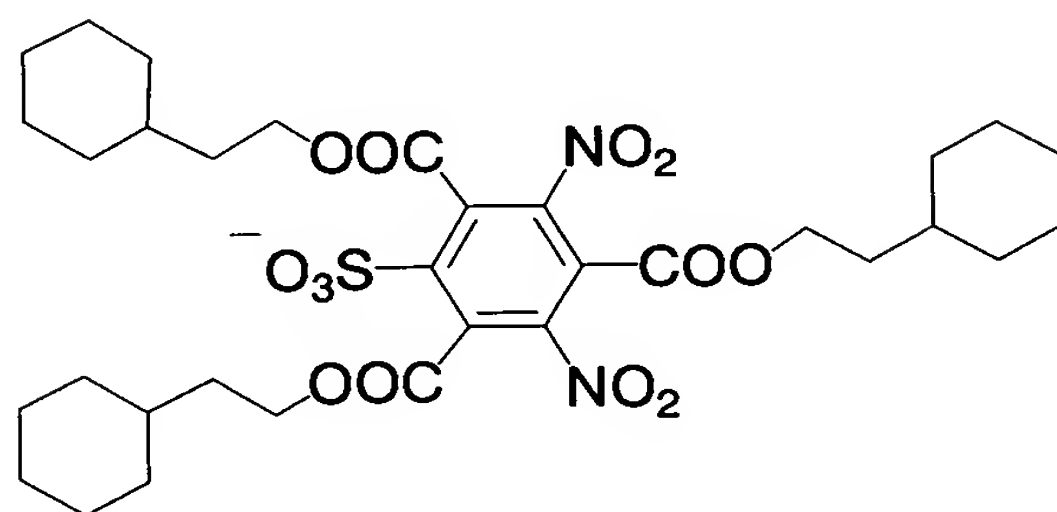
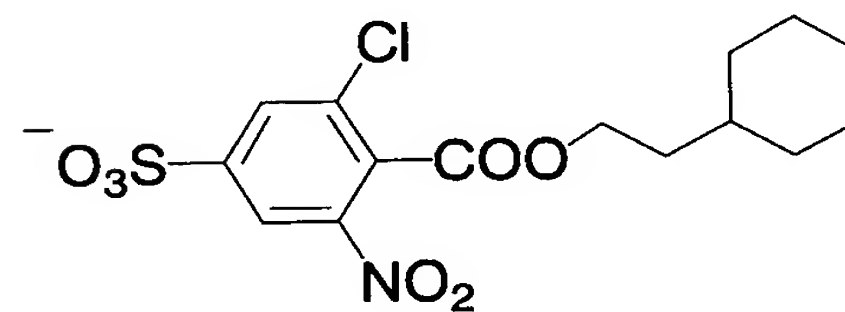
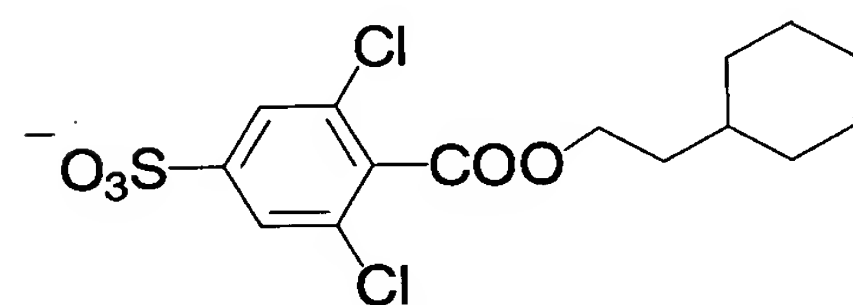
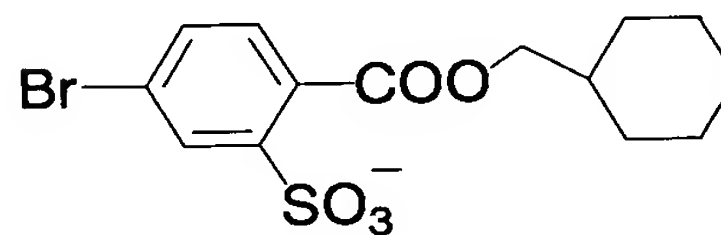
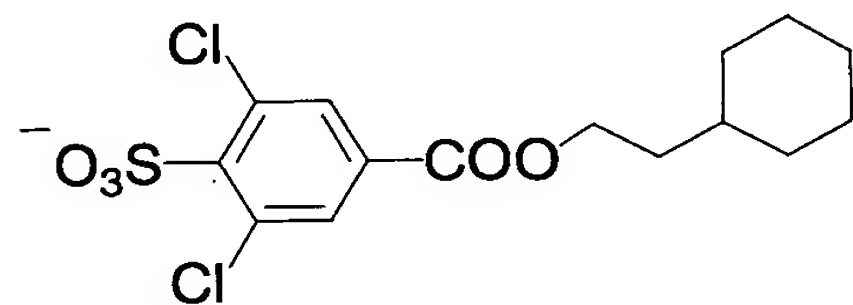
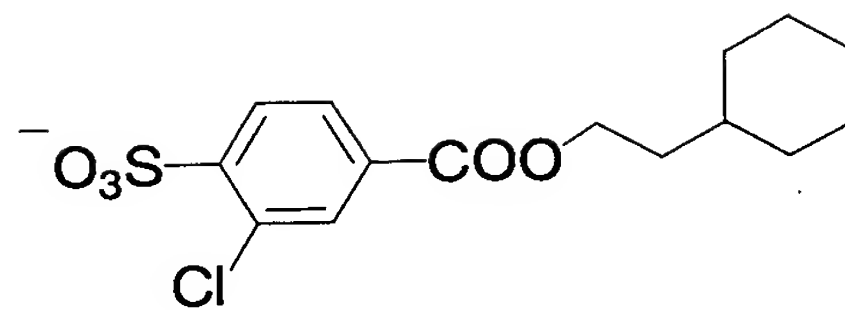
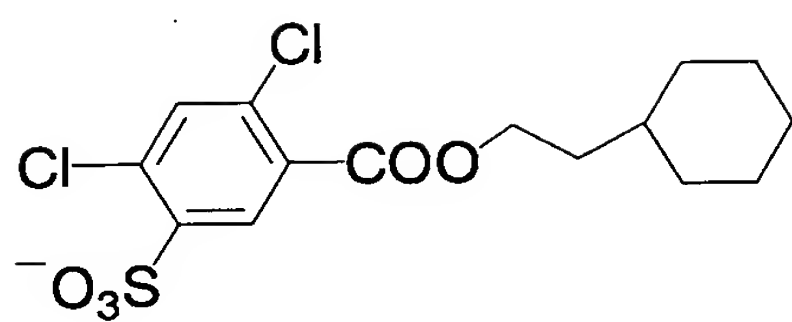
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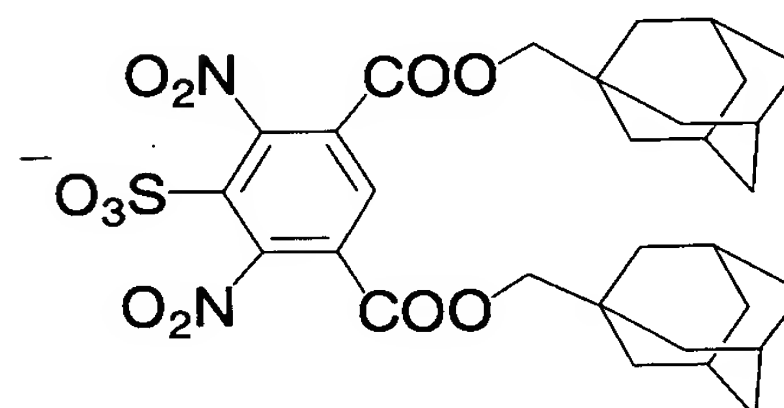
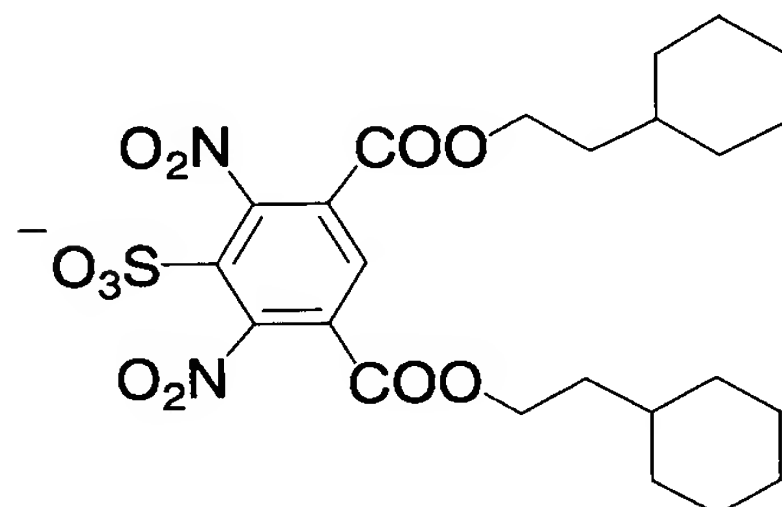
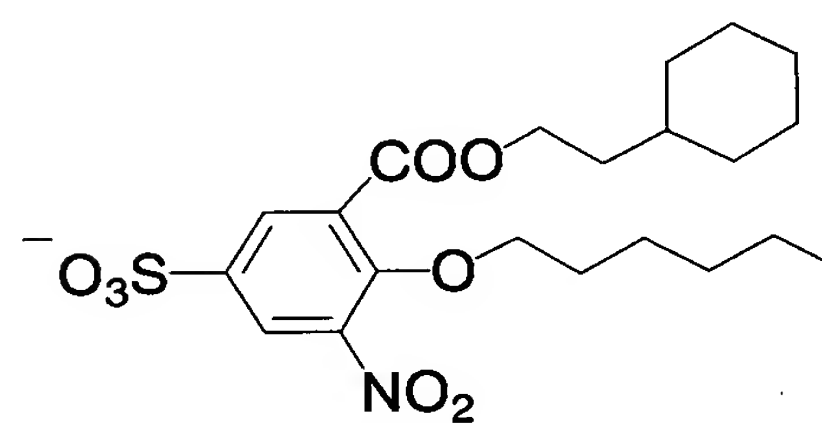
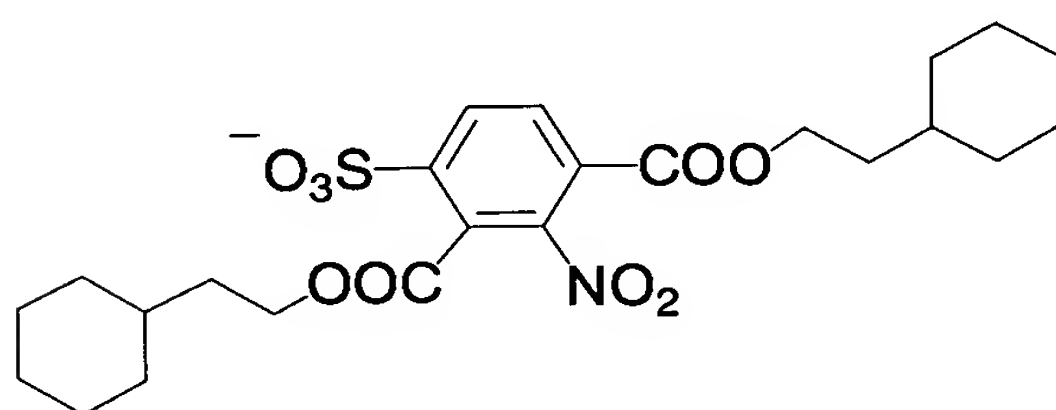
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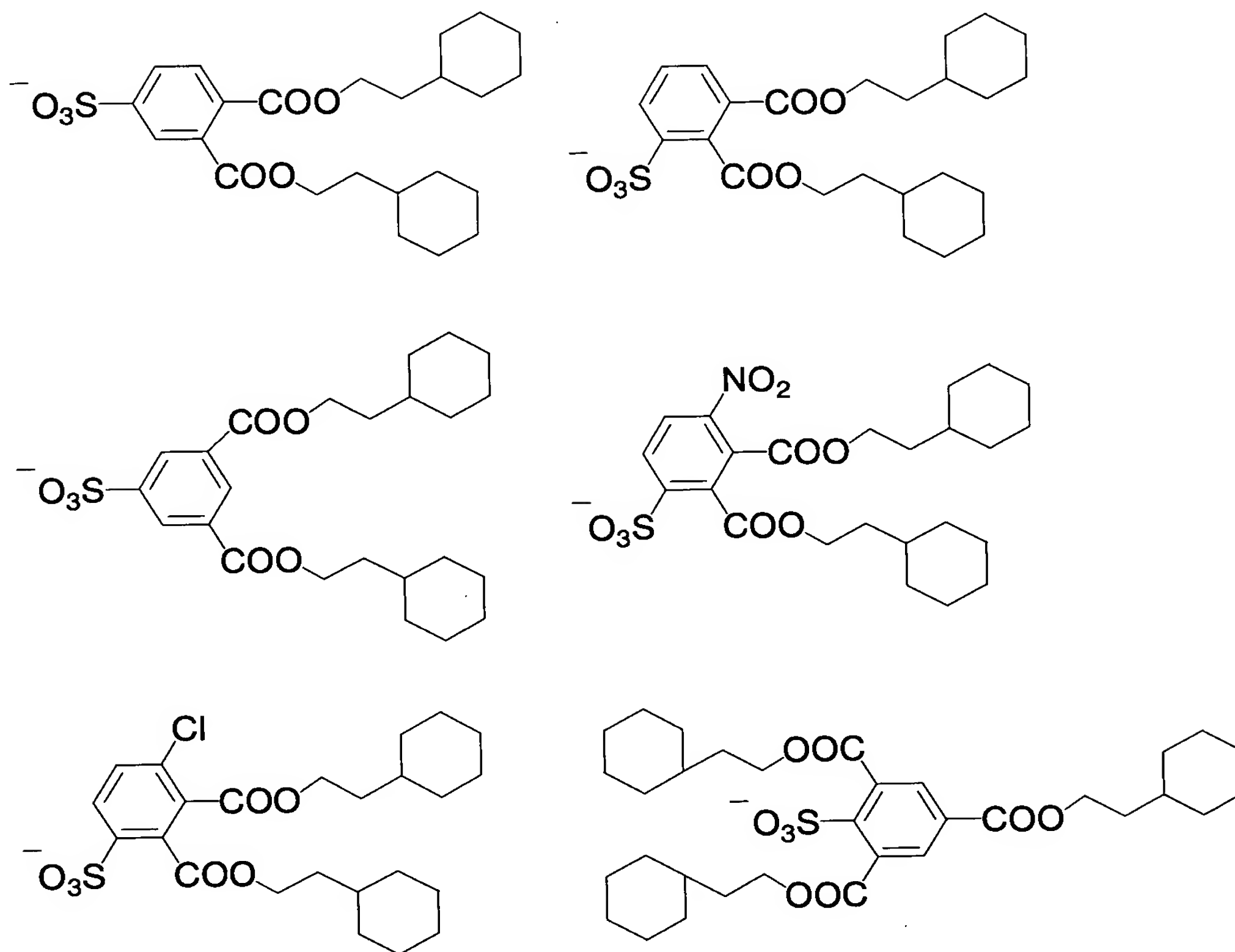
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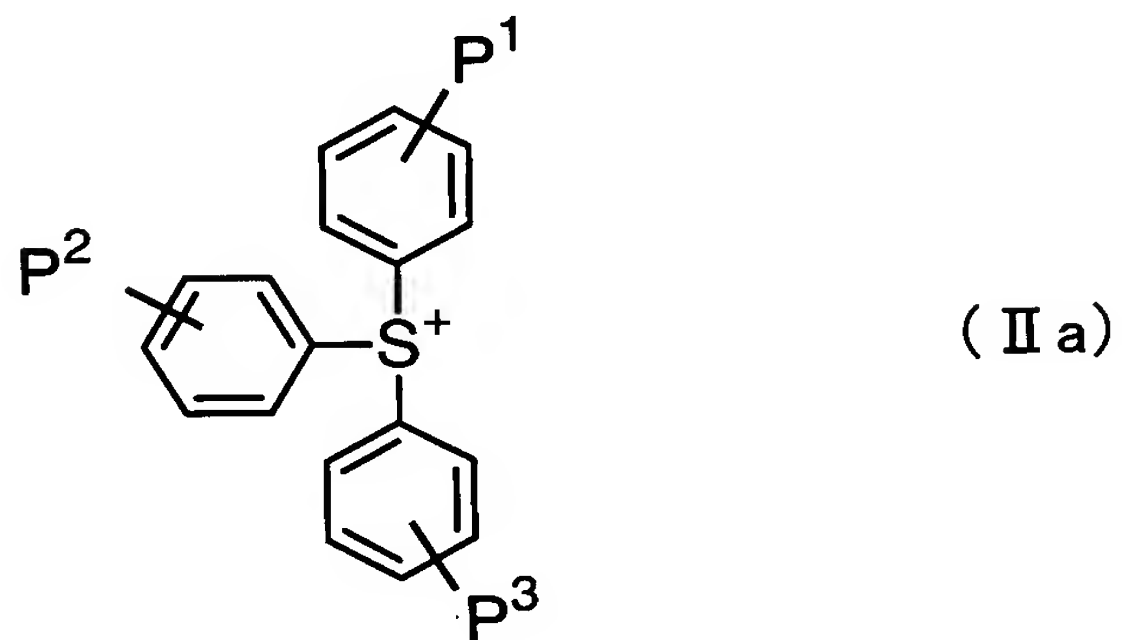


[0017]



5 [0018]

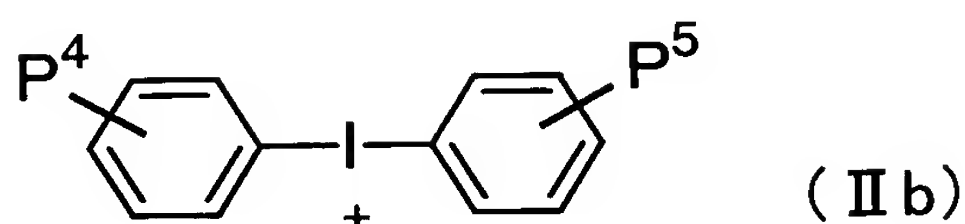
Examples of the salt of the formula (I) include salts wherein A^+ is the formula (IIa), (IIb), (IIc) or (IId):



wherein P^1 , P^2 and P^3 each independently represent hydrogen, hydroxyl, alkyl

having 1 to 6 carbon atoms or alkoxy having 1 to 6 carbon atoms;

[0019]



wherein P^4 and P^5 each independently represent hydrogen, hydroxyl, alkyl

5 having 1 to 6 carbon atoms or alkoxy having 1 to 6 carbon atoms;

[0020]

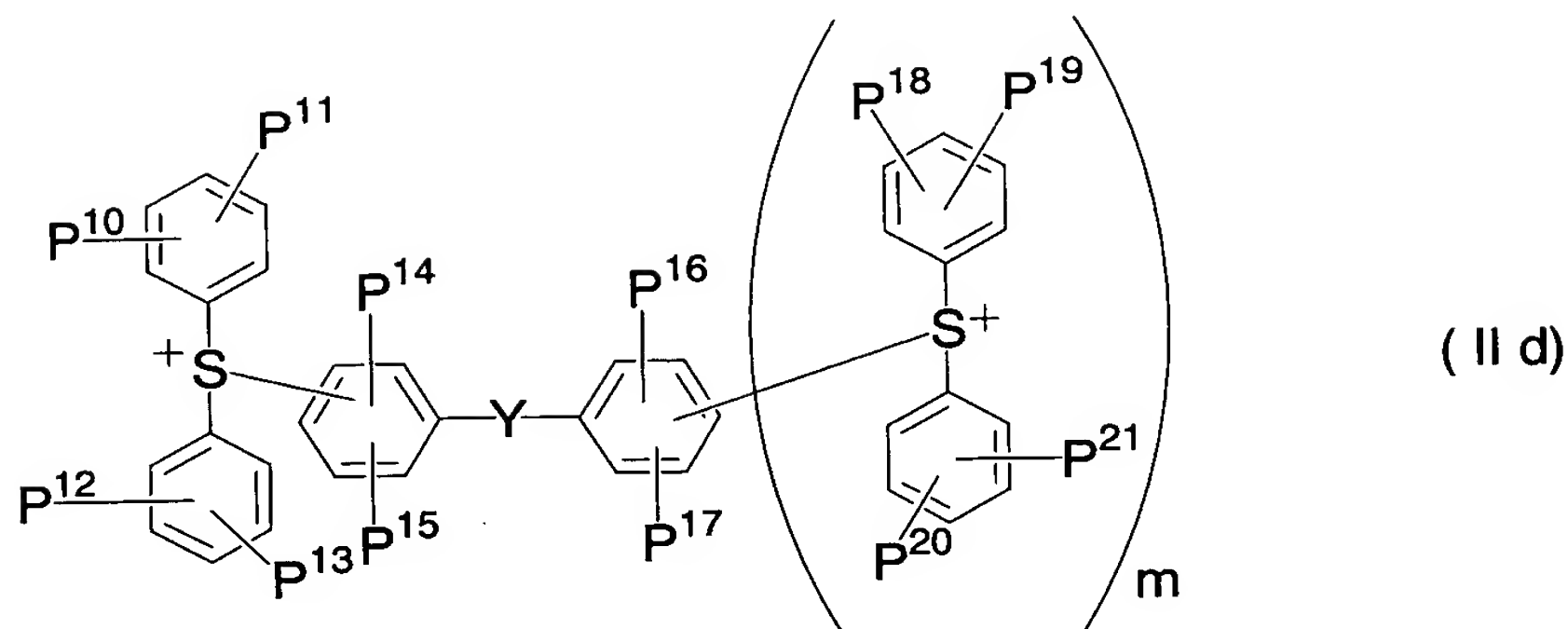


wherein P^6 and P^7 each independently represent alkyl having 1 to 6 carbon atoms or cycloalkyl having 3 to 10 carbon atoms, or P^6 and P^7 bond to form alicyclic

10 hydrocarbon group having 3 to 7 carbon atoms, said alicyclic hydrocarbon group may have ketone group, and at least one $-CH_2-$ in the alicyclic hydrocarbon group may be substituted by oxygen or sulfur; P^8 represents hydrogen, P^9 represents alkyl having 1 to 6 carbon atoms, cycloalkyl having 3 to 10 carbon atoms or aromatic ring group optionally substituted, or P^8 and P^9 bond to form

15 alicyclic hydrocarbon group;

[0021]



wherein P^{10} to P^{21} each independently represent hydrogen, hydroxyl, alkyl having 1 to 6 carbon atoms or alkoxy having 1 to 6 carbon atoms, Y represents sulfur or oxygen, and m represents 0 or 1.

5 [0022]

In the formula (IIa), P^1 , P^2 and P^3 each independently represent hydrogen, hydroxyl, alkyl having 1 to 6 carbon atoms or alkoxy having 1 to 6 carbon atoms, and the alkyl and alkoxy may be linear or branched in the case of 3 or more carbon atoms.

10

In the formula (IIb), P^4 and P^5 each independently represent hydrogen, hydroxyl, alkyl having 1 to 6 carbon atoms or alkoxy having 1 to 6 carbon atoms, and the alkyl and alkoxy may be linear or branched in the case of 3 or more carbon atoms.

In P^1 , P^2 , P^3 , P^4 and P^5 , specific examples of the alkyl include methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, pentyl, hexyl and the like, and examples of the alkoxy include methoxy, ethoxy, propoxy, butoxy and the like.

15

[0023]

In the formula (IIc), P^6 and P^7 each independently represent alkyl having 1 to 6 carbon atoms or cycloalkyl having 3 to 10 carbon atoms, or alicyclic

hydrocarbon group having 3 to 7 carbon atoms. Said alicyclic hydrocarbon group may have carbonyl group. At least one $-\text{CH}_2-$ in the alicyclic hydrocarbon group may be substituted by oxygen or sulfur.

P^8 represents hydrogen and P^9 represents alkyl having 1 to 6 carbon atoms, cycloalkyl having 3 to 10 carbon atoms or aromatic ring group optionally substituted, or P^8 and P^9 bond to form alicyclic hydrocarbon group.

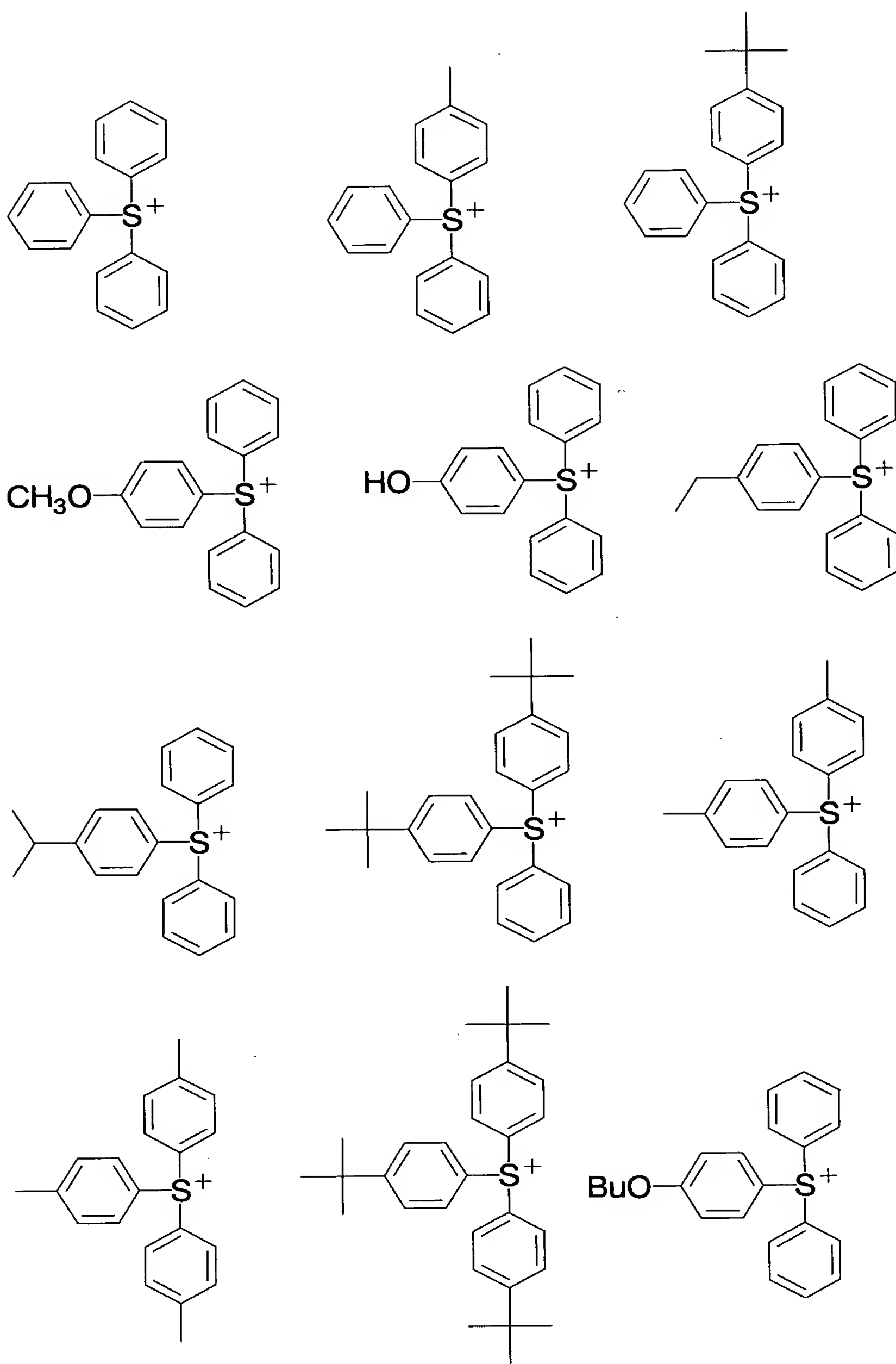
Specific examples of the alkyl include methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, pentyl, hexyl and the like, and specific examples of the cycloalkyl include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and the like.

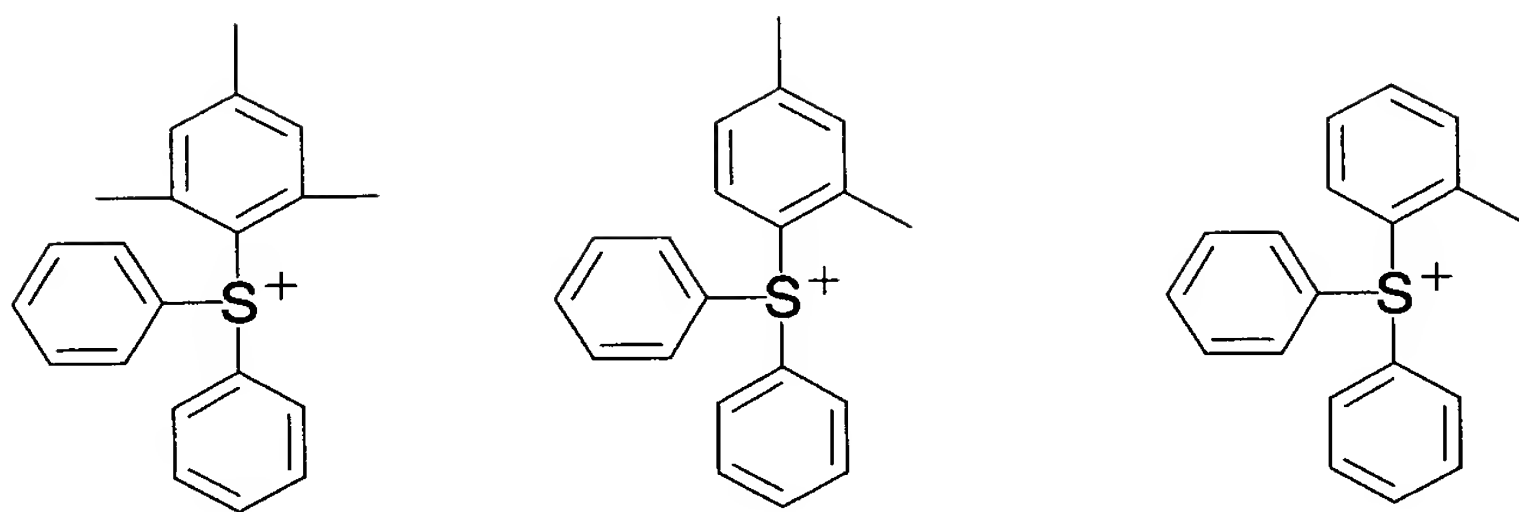
[0024]

In the formula (IId), P^{10} to P^{21} each independently represent hydrogen, hydroxyl, alkyl having 1 to 6 carbon atoms or alkoxy having 1 to 6 carbon atoms. The alkyl and alkoxy may be linear or branched in the case of 3 or more carbon atoms. Specific examples of the alkyl include methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, pentyl, hexyl and the like, and examples of the alkoxy include methoxy, ethoxy, propoxy, butoxy and the like. Y represents sulfur or oxygen. m represents 0 or 1.

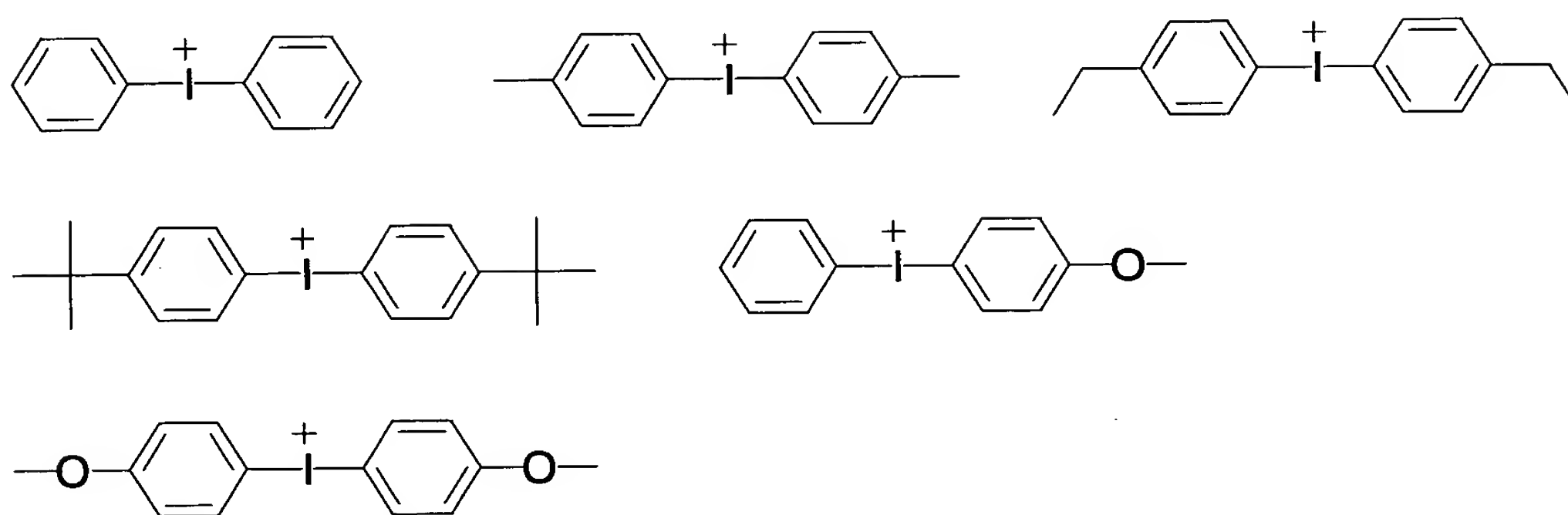
[0025]

Specific examples of the counter ion represented by A^+ in the salt of the formula (I) include the followings:



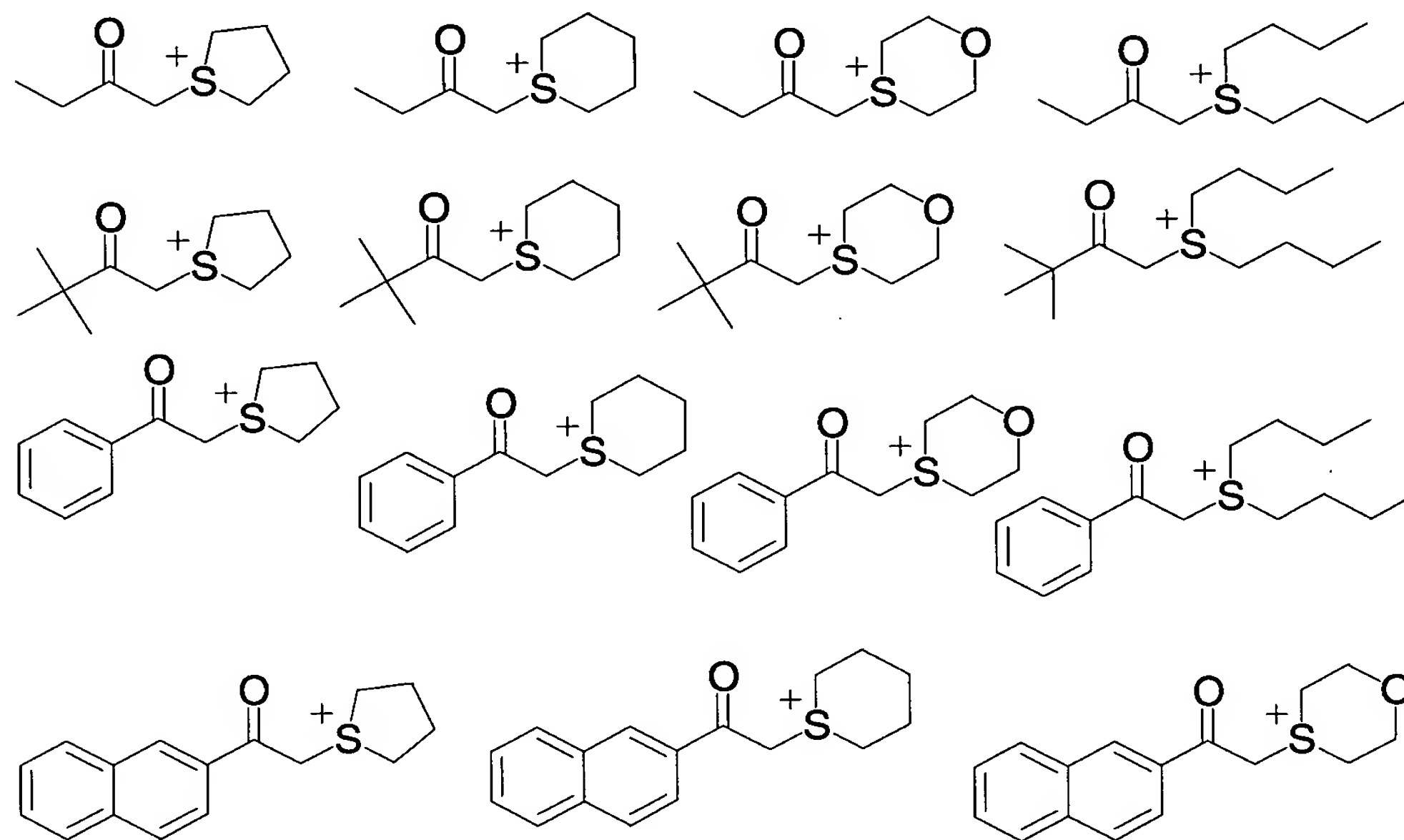


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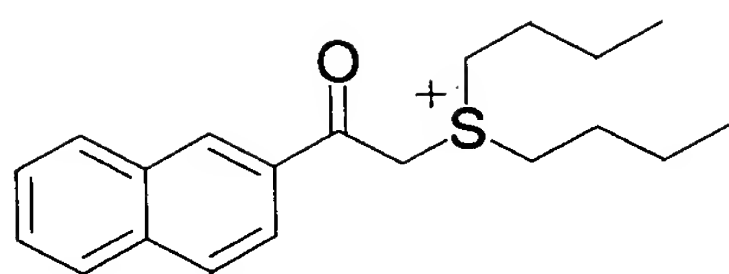


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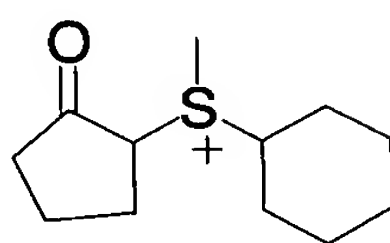
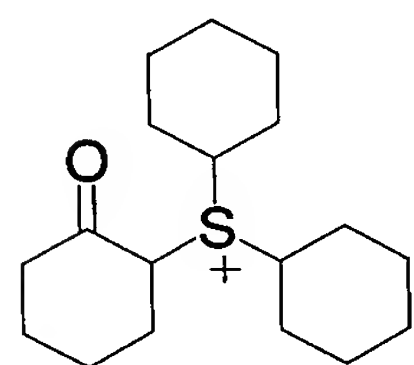
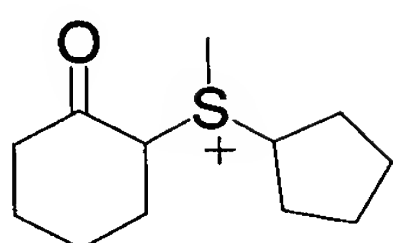
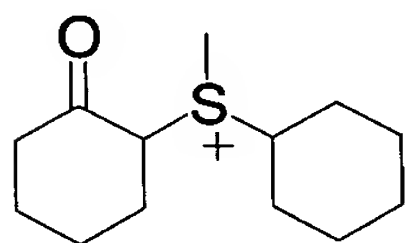
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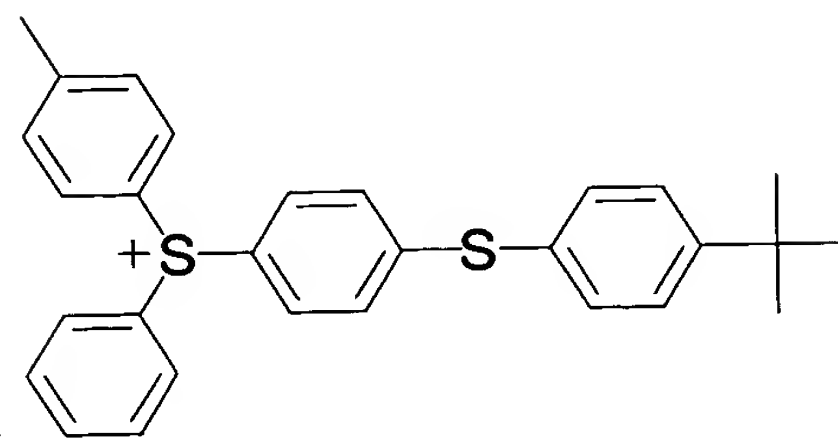
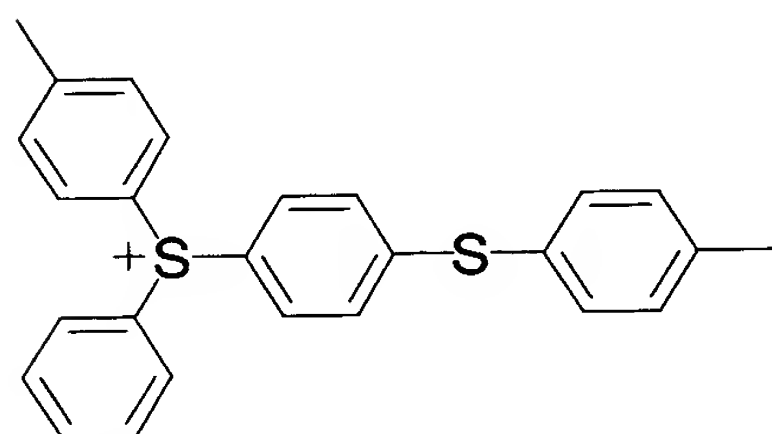
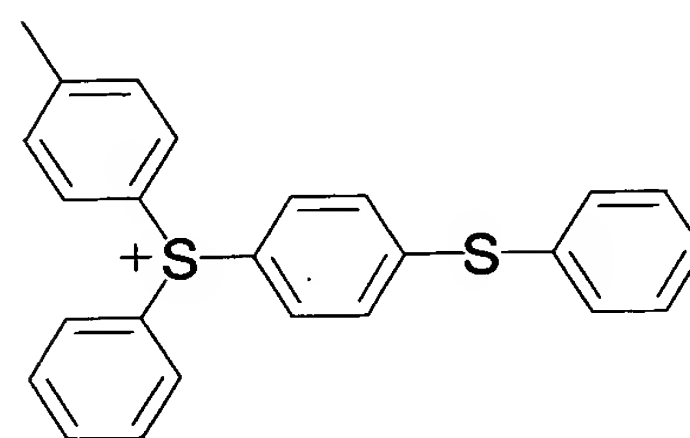
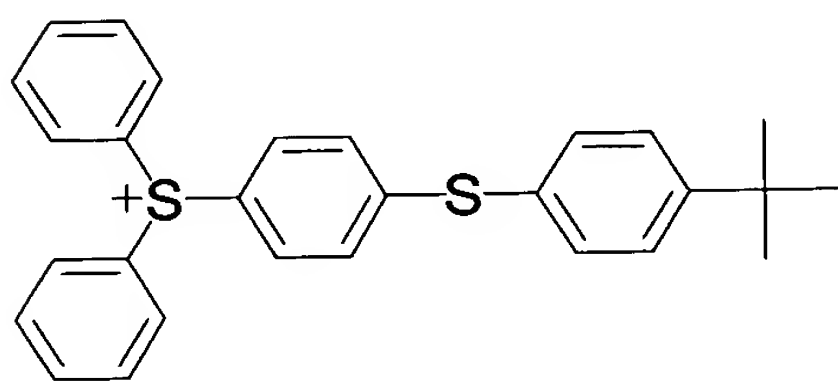
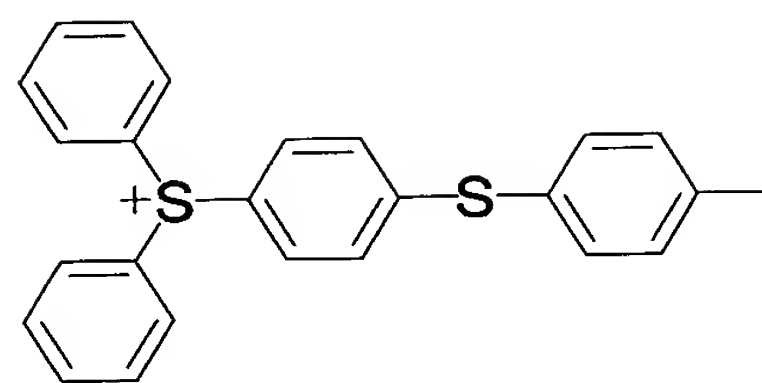
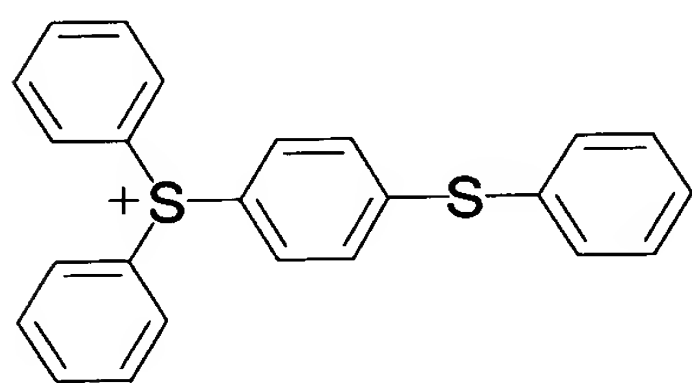
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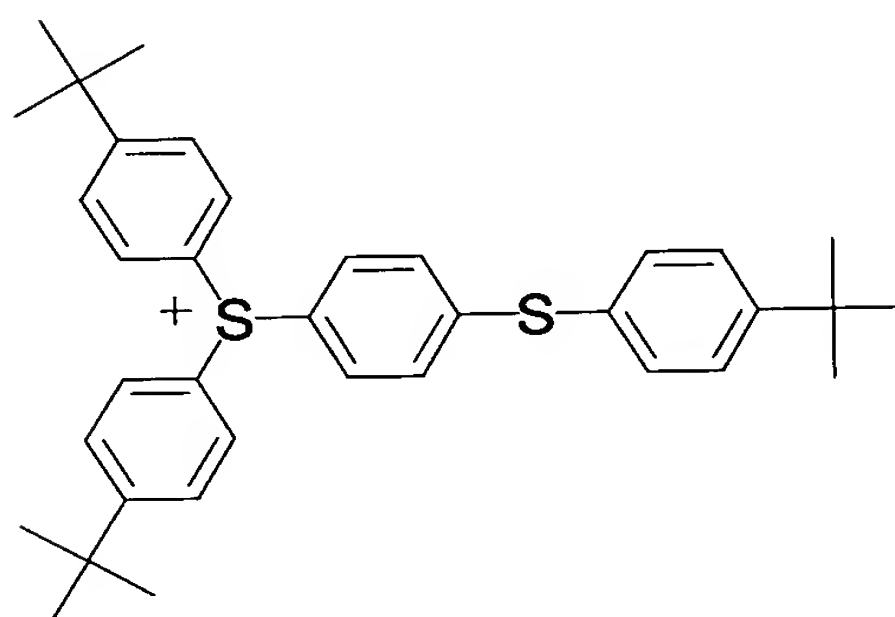
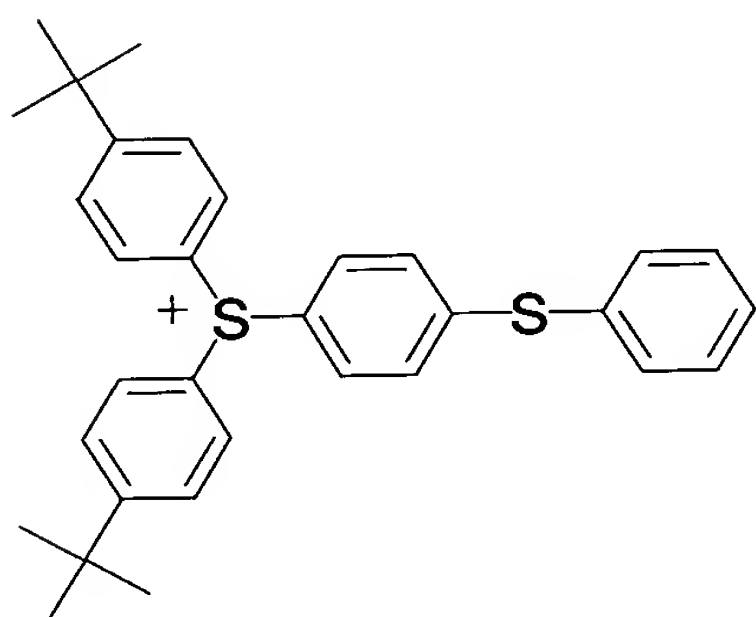
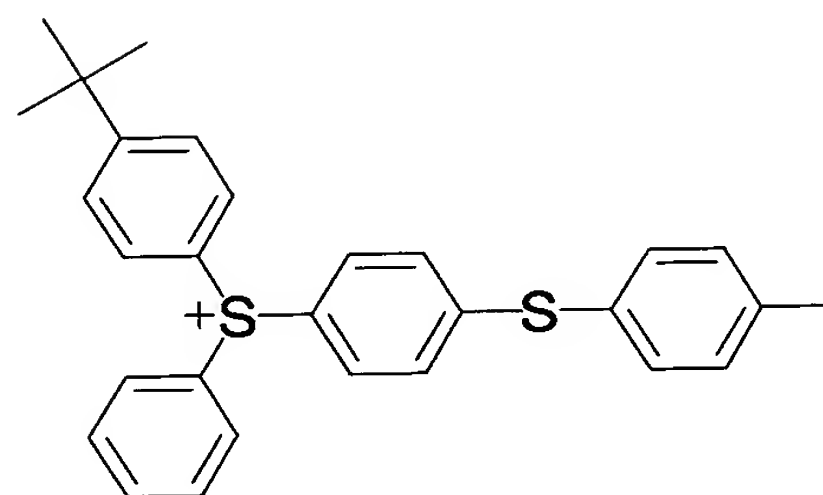
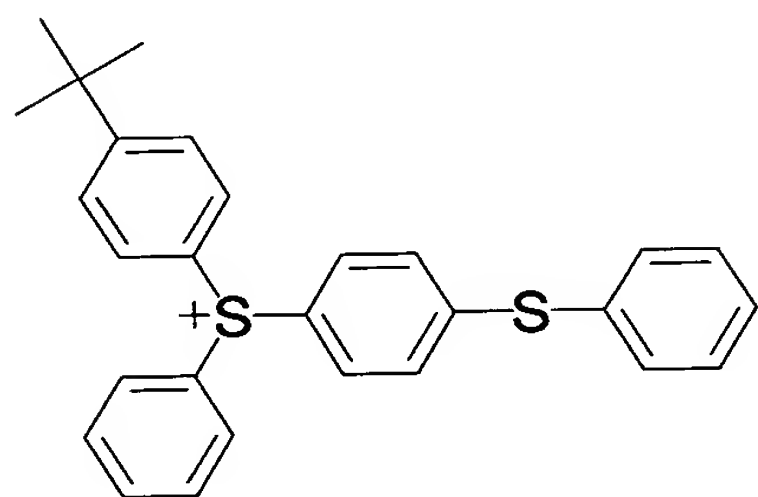
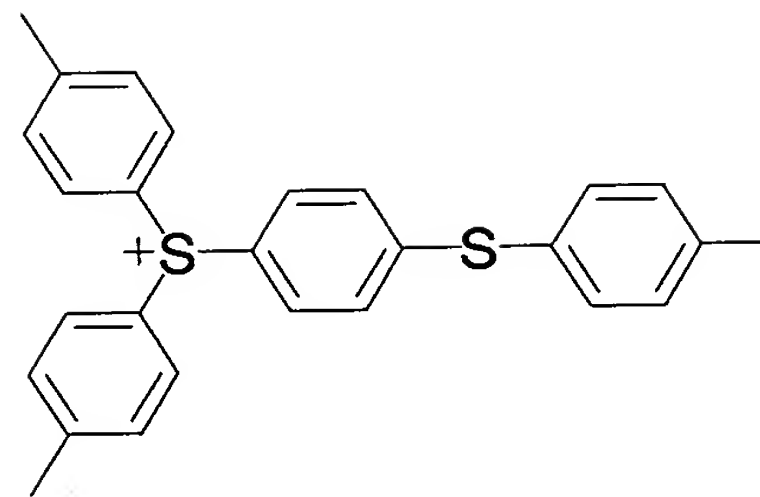
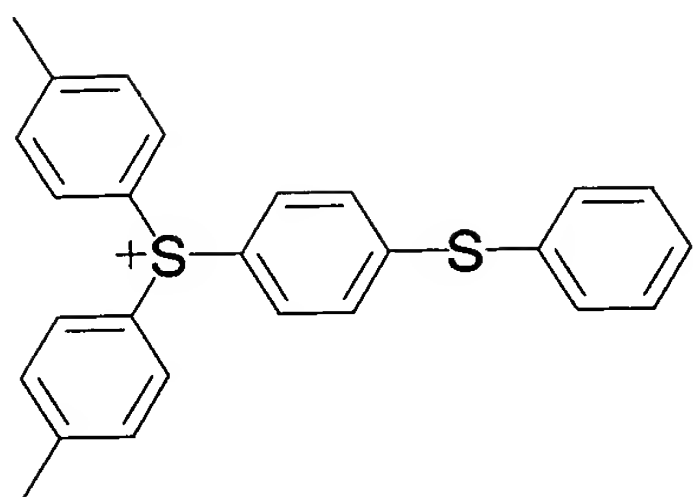


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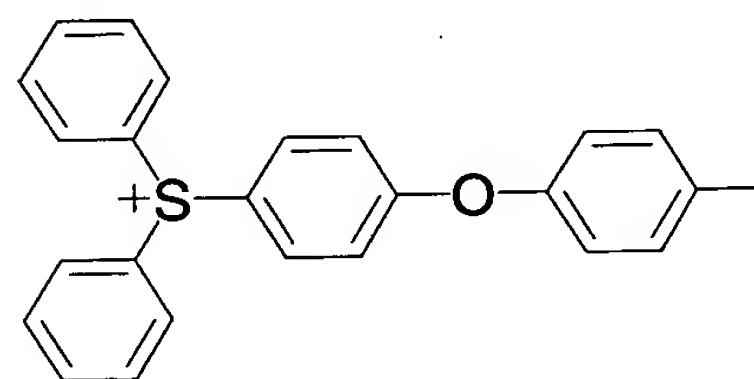
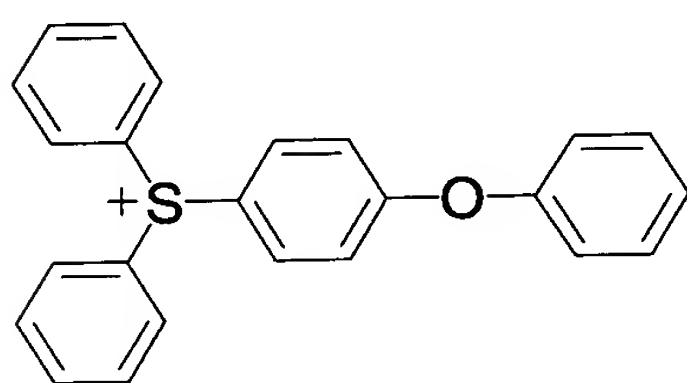


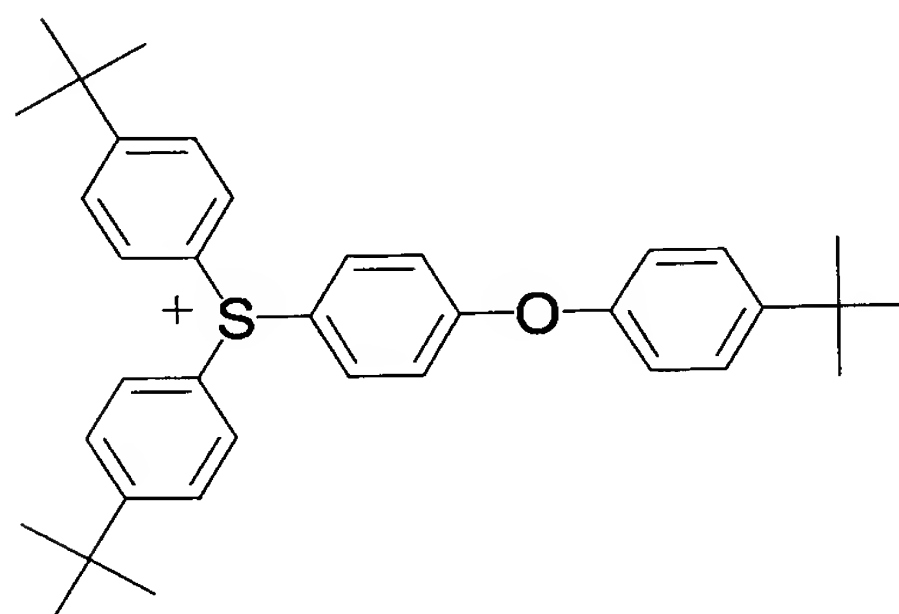
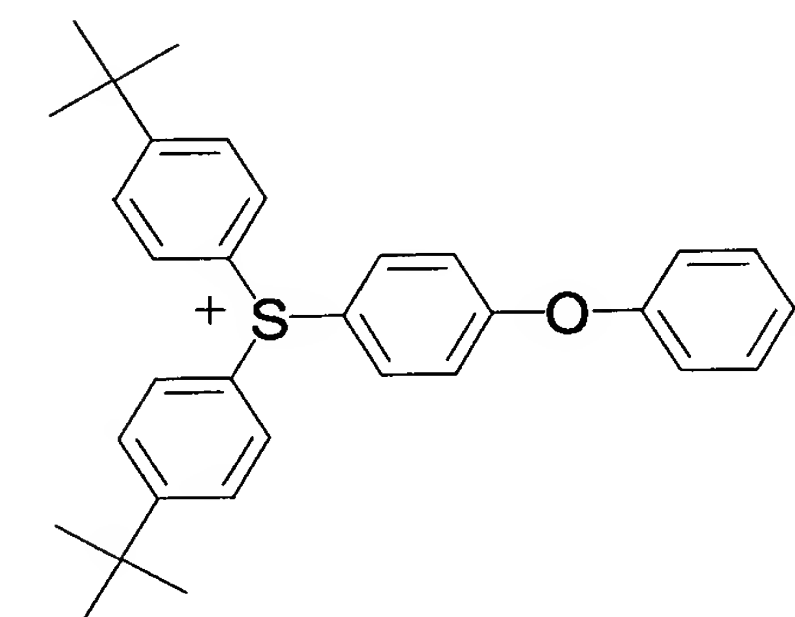
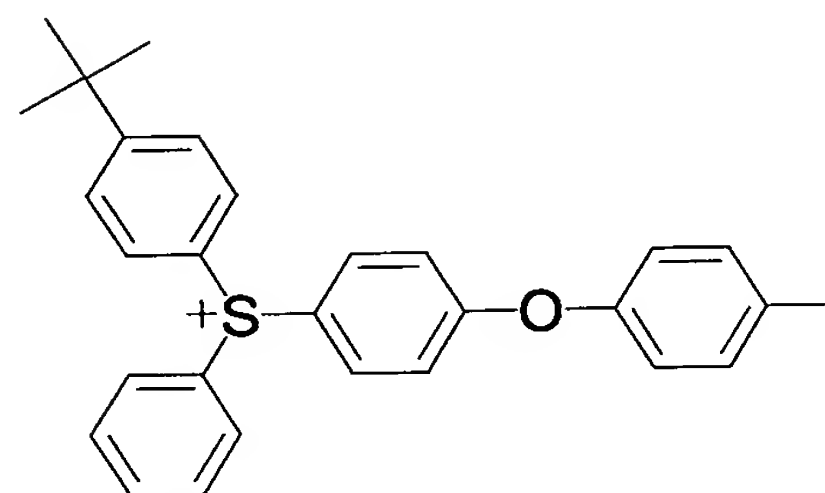
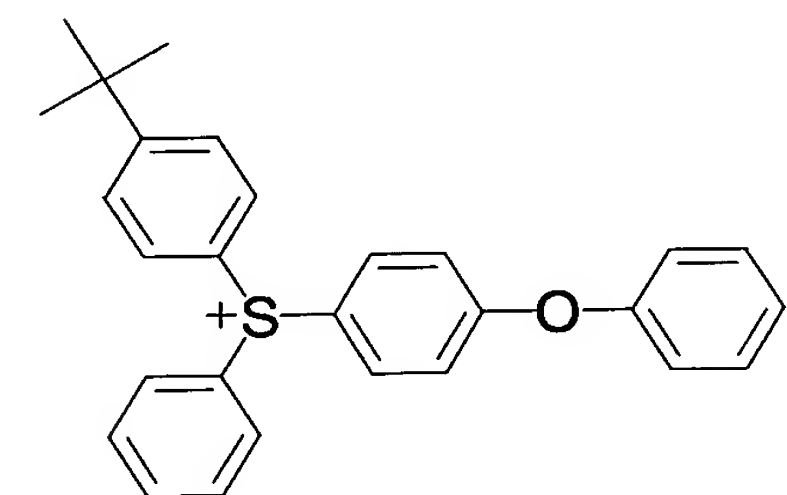
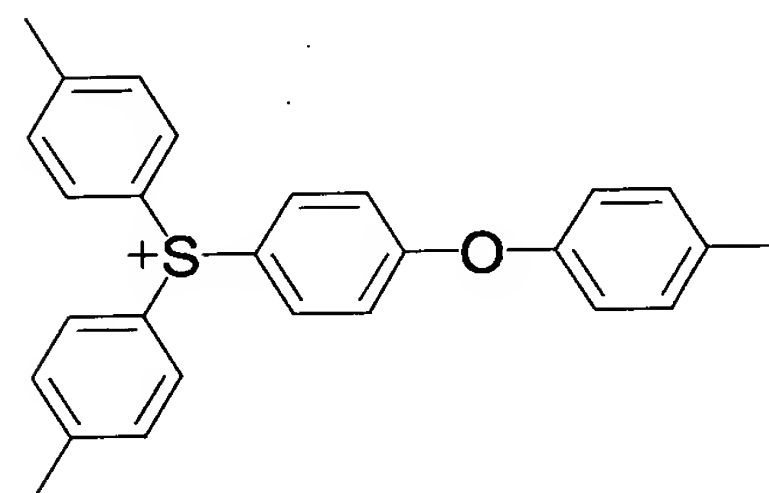
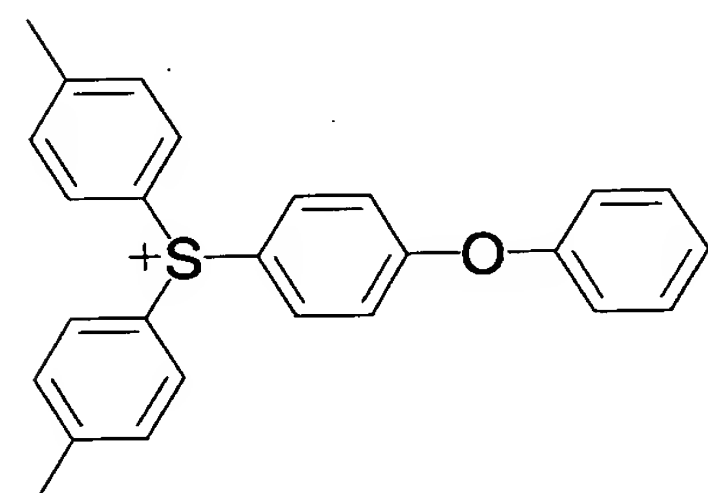
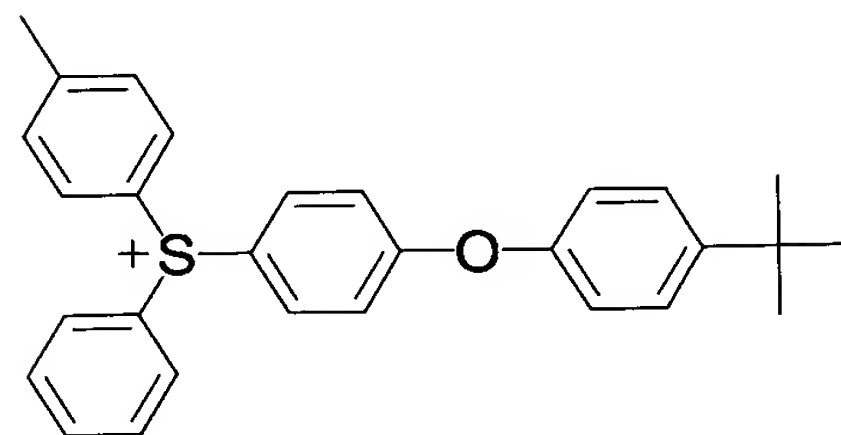
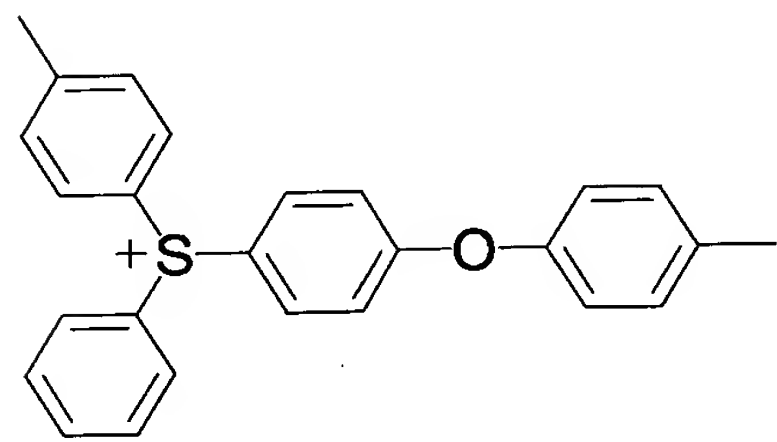
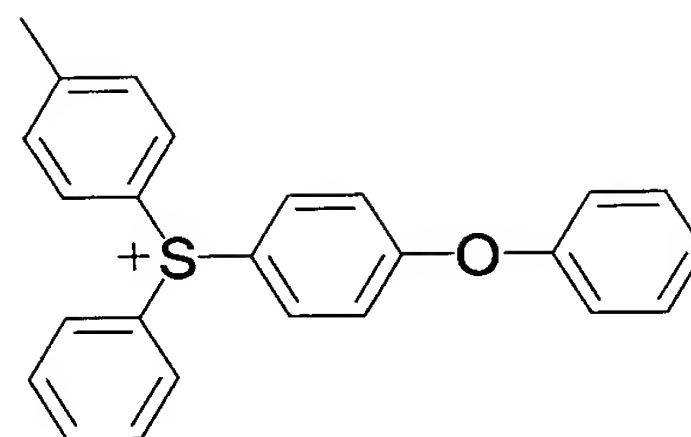
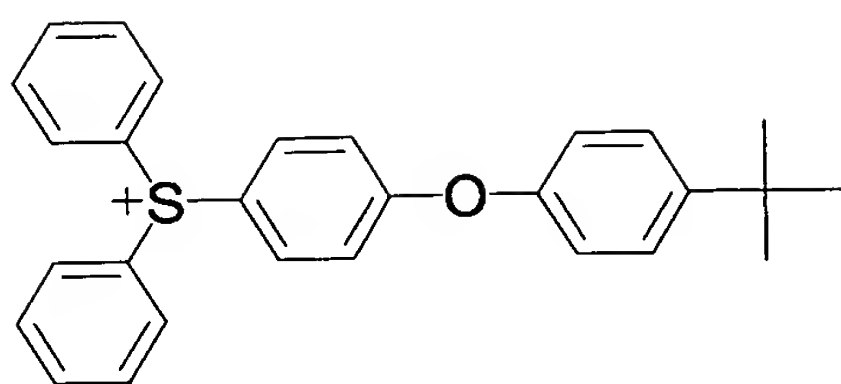
5 [0029]



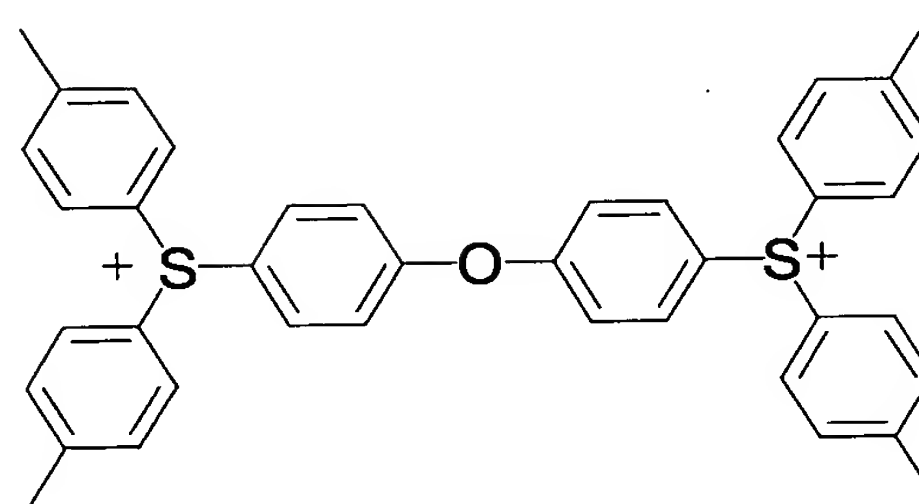
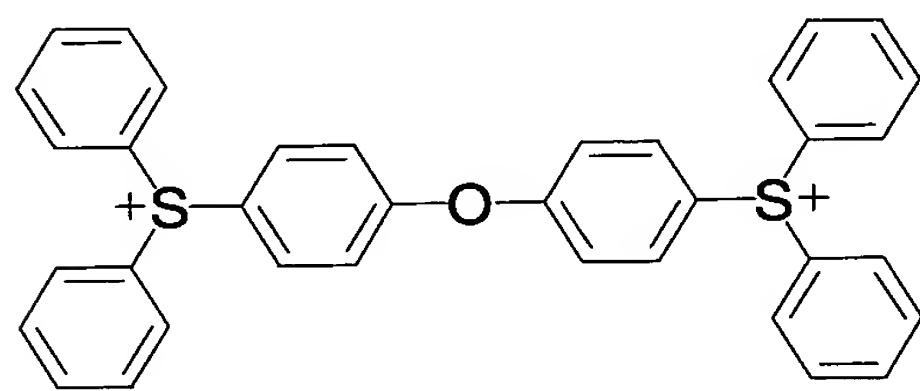
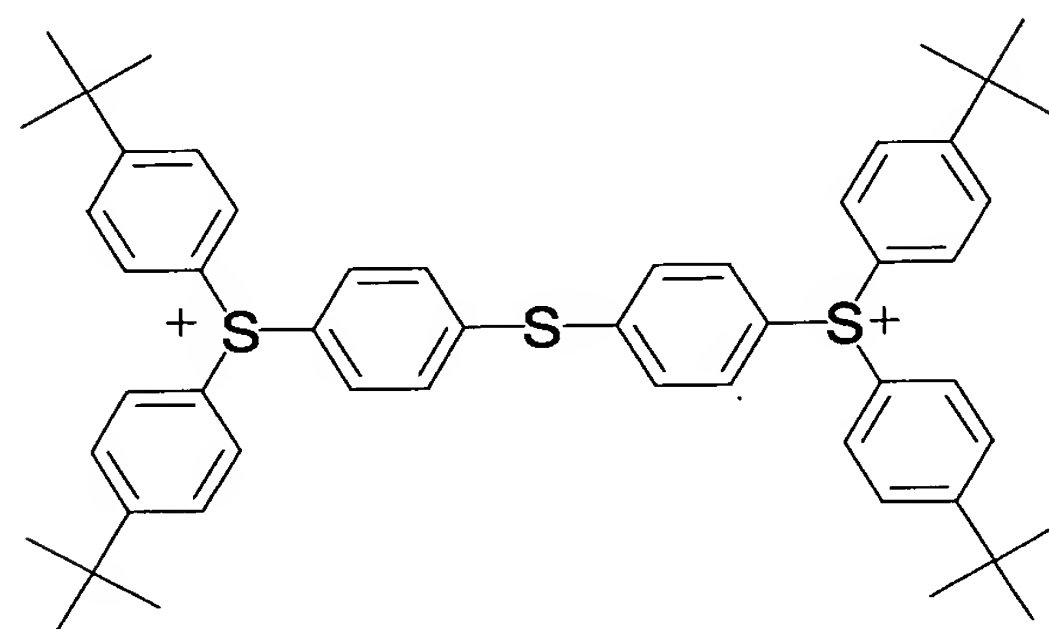
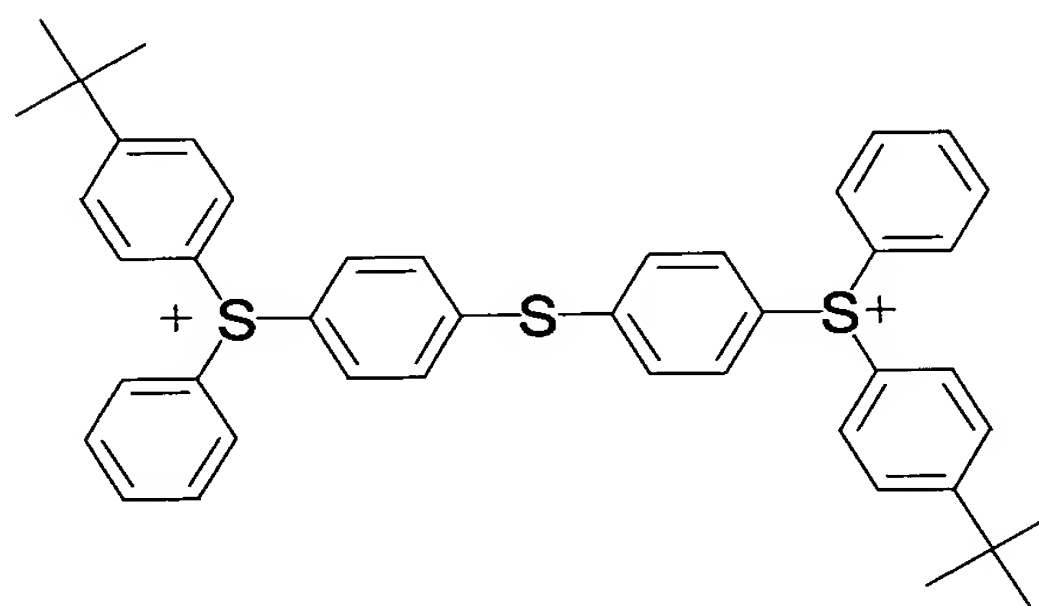
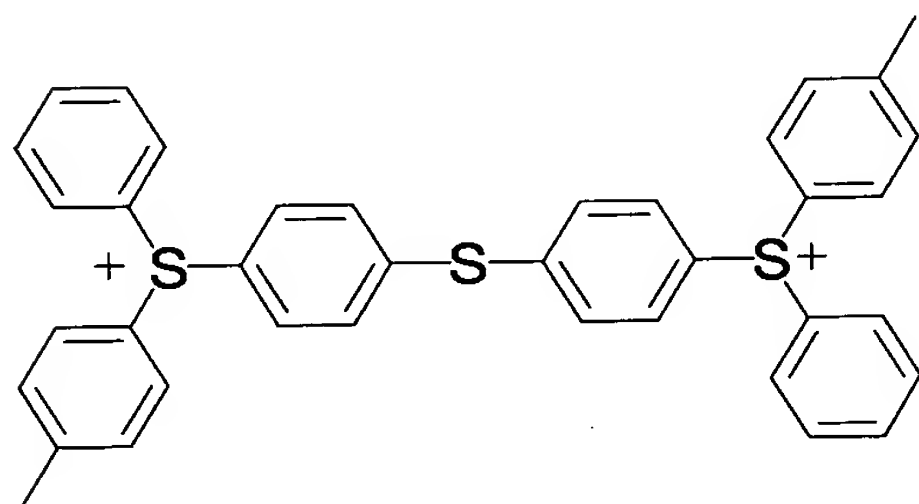
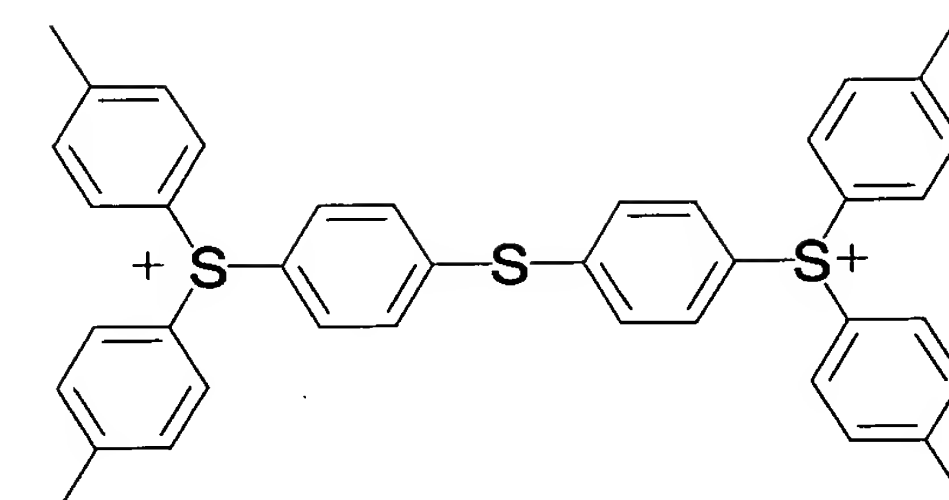
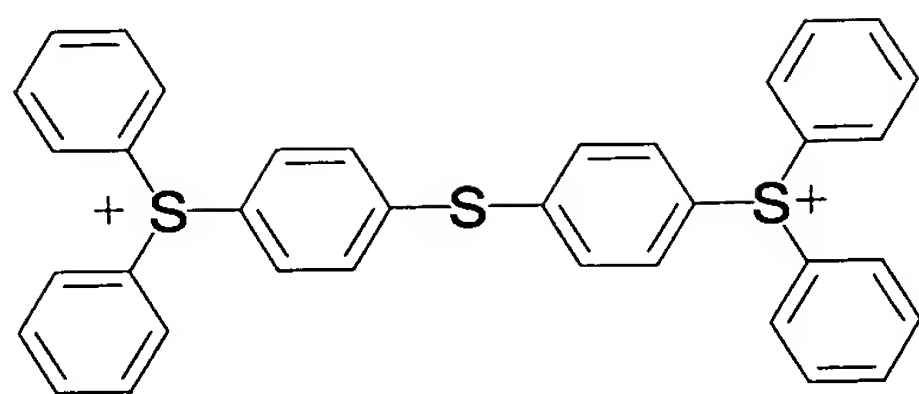


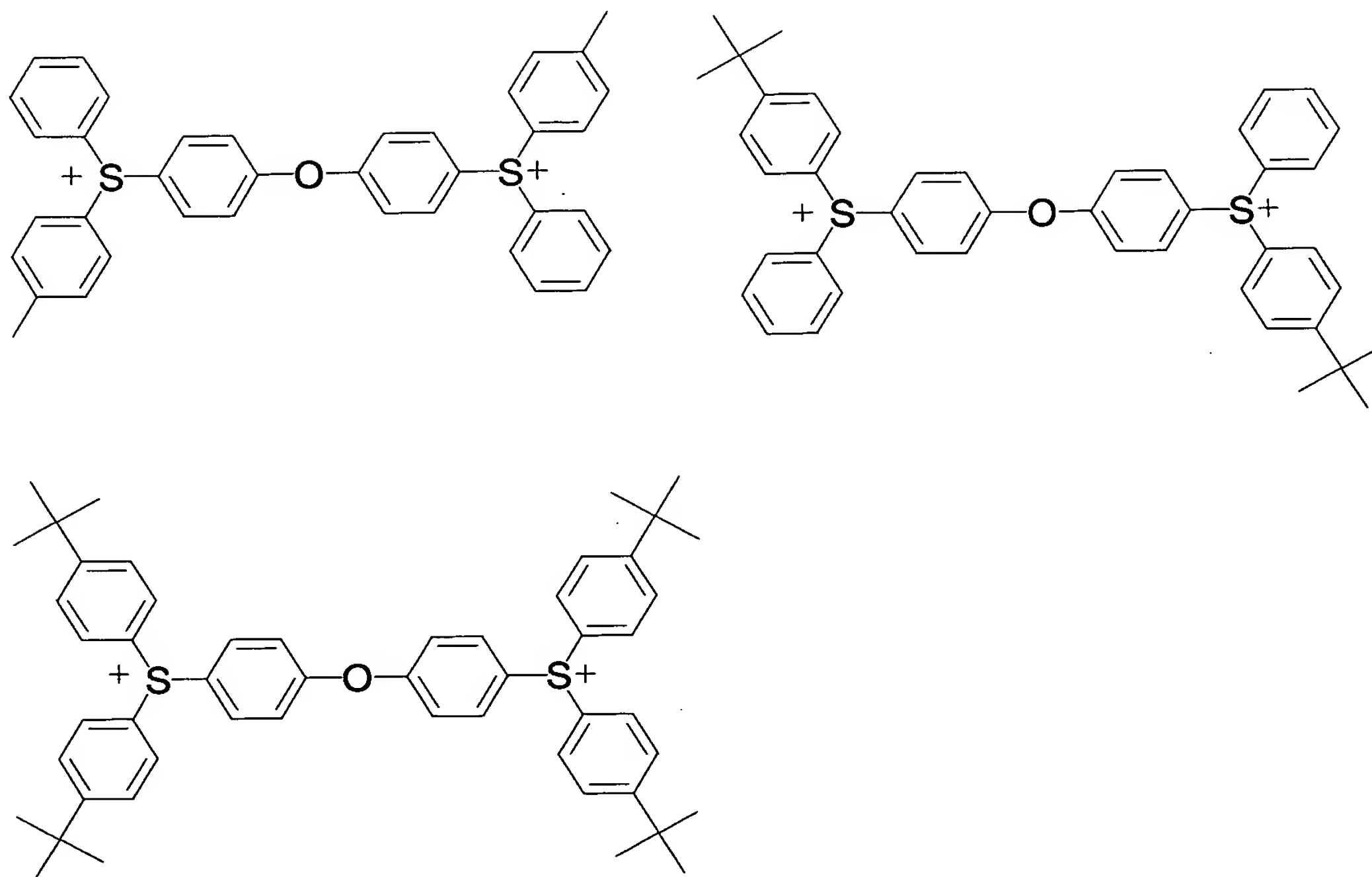
[0030]





[0031]





[0032]

The chemical amplification type positive resist composition of the present invention comprises resin which contains a structural unit having an acid labile group and which itself is insoluble or poorly soluble in an alkali aqueous solution but becomes soluble in an alkali aqueous solution by the action of an acid, and the salt represented by the formula (I) described above.

[0033]

As salt of the formula (I) in the present composition, salt wherein A^+ is the formula (IIa), salt wherein A^+ is the formula (IIb), salt wherein A^+ is the formula (IIc) and salt wherein A^+ is the formula (IIa) are preferred.

In the formula (IIa), P^1 , P^2 and P^3 each independently represent hydrogen, hydroxyl, alkyl having 1 to 6 carbon atoms or alkoxy having 1 to 6 carbon atoms, and the alkyl and alkoxy may be linear or branched in the case of 3 or more

carbon atoms.

In the formula (IIb), P^4 and P^5 each independently represent hydrogen, hydroxyl, alkyl having 1 to 6 carbon atoms or alkoxy having 1 to 6 carbon atoms, and the alkyl and alkoxy may be linear or branched in the case of 3 or more
5 carbon atoms.

In P^1 , P^2 , P^3 , P^4 and P^5 , specific examples of the alkyl include methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, pentyl, hexyl and the like, and examples of the alkoxy include methoxy, ethoxy, propoxy, butoxy and the like.

[0034]

10 In the formula (IIc), P^6 and P^7 each independently represent alkyl having 1 to 6 carbon atoms or cycloalkyl having 3 to 10 carbon atoms, or P^6 and P^7 bond to form alicyclic hydrocarbon group having 3 to 7 carbon atoms. Said alicyclic hydrocarbon group may have carbonyl group. At least one $-CH_2-$ in the alicyclic hydrocarbon group may be substituted by oxygen or sulfur.

15 P^8 represents hydrogen and P^9 represents alkyl having 1 to 6 carbon atoms, cycloalkyl having 3 to 10 carbon atoms or aromatic ring group optionally substituted, or P^8 and P^9 bond to form alicyclic hydrocarbon group.

Specific examples of the alkyl include methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, pentyl, hexyl and the like, and specific examples of the
20 cycloalkyl include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and the like.

[0035]

In the formula (IId), P^{10} to P^{21} each independently represent hydrogen, hydroxyl, alkyl having 1 to 6 carbon atoms or alkoxy having 1 to 6 carbon atoms.

The alkyl and alkoxy may be linear or branched in the case of 3 or more carbon atoms. Specific examples of the alkyl include methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, pentyl, hexyl and the like, and examples of the alkoxy include methoxy, ethoxy, propoxy, butoxy and the like. Y represents sulfur or oxygen.

5 m represents 0 or 1.

[0036]

Next, resin components constituting the present composition will be explained. The resin used in the present composition contains a structural unit having an acid-labile group. The resin for the chemical amplification type
10 positive resist composition is insoluble or poorly soluble itself in alkali aqueous solution and shows partial dissociation of groups by the action of an acid to become soluble in alkali aqueous solution after the dissociation. The acid-labile group can be selected from conventionally known various groups.

Specifically, various esters of carboxylic acids are mentioned as the
15 acid-labile group, and examples thereof include alky esters such as methyl ester and tert-butyl ester; acetal type esters such as methoxymethyl ester, ethoxymethyl ester, 1-ethoxyethyl ester, 1-isobutoxyethyl ester, 1-isopropoxyethyl ester, 1-ethoxypropyl ester, 1-(2-methoxyethoxy)ethyl ester, 1-(2-acetoxyethoxy)ethyl ester, 1-[2-(1-adamantyloxy)ethoxy]ethyl ester,
20 1-[2-(1-adamantanecarbonyloxy)ethoxy]ethyl ester, tetrahydro-2-furyl ester and tetrahydro-2-pyranyl ester; alicyclic esters such as isobornyl ester, 2-alkyl-2-adamantyl ester, 1-(1-adamantyl)-1-alkylalkyl ester, and the like.

Monomers leading to structural units having such ester of carboxylic acid may be (meth)acryl-based monomers such as methacrylates and acrylates,

or those obtained by bonding of a ester group of carboxylic acid to alicyclic monomer such as norbornenecarboxylate, tricyclodecenecarboxylate and tetracyclodecenecarboxylate.

[0037]

5 Among the above-mentioned monomers, it is preferable to use those having a bulky group containing alicyclic group such as, for example, 2-alkyl-2-adamantyl and 1-(1-adamantyl)-1-alkylalkyl, as the group dissociated by the action of an acid, since excellent resolution is obtained.

Examples of such monomer containing a bulky group include
10 2-alkyl-2-adamantyl (meth)acrylate, 1-(1-adamantyl)-1-alkylalkyl (meth)acrylate, 2-alkyl-2-adamantyl 5-norbornene-2-carboxylate, 1-(1-adamantyl)-1-alkylalkyl 5-norbornene-2-carboxylate, and the like.

Particularly when 2-alkyl-2-adamantyl (meth)acrylate or 2-alkyl-2-adamantyl α -chloroacrylate is used as the monomer, it is preferred
15 because excellent resolution is obtained. Typical examples of such 2-alkyl-2-adamantyl (meth)acrylate and 2-alkyl-2-adamantyl α -chloroacrylate include 2-methyl-2-adamantyl acrylate, 2-methyl-2-adamantyl methacrylate, 2-ethyl-2-adamantyl acrylate, 2-ethyl-2-adamantyl methacrylate, 2-n-butyl-2-adamantyl acrylate, 2-methyl-2-adamantyl α -chloroacrylate,
20 2-ethyl-2-adamantyl α -chloroacrylate and the like. When particularly 2-ethyl-2-adamantyl (meth)acrylate or 2-ethyl-2-adamantyl α -chloroacrylate is used, it is preferred because balance between sensitivity and heat resistance is excellent. In the present invention, other monomer having group dissociated by the action of an acid may be used together, if necessary.

[0038]

2-alkyl-2-adamantyl (meth)acrylate can usually be produced by reacting 2-alkyl-2-adamantanol or metal salt thereof with an acrylic halide or methacrylic halide.

5 [0039]

The resin used for the present composition can also contain, in addition to the above-mentioned structural units having an acid-labile group, other structural units not dissociated or not easily dissociated by the action of an acid. Examples of such other structural units which can be contained include
10 structural units of monomers having a free carboxyl group such as acrylic acid and methacrylic acid, structural units of aliphatic unsaturated dicarboxylic anhydrides such as maleic anhydride and itaconic anhydride, structural unit of 2-norbornene, structural unit of (meth)acrylonitrile, structural unit of various (meth)acrylate, and the like.

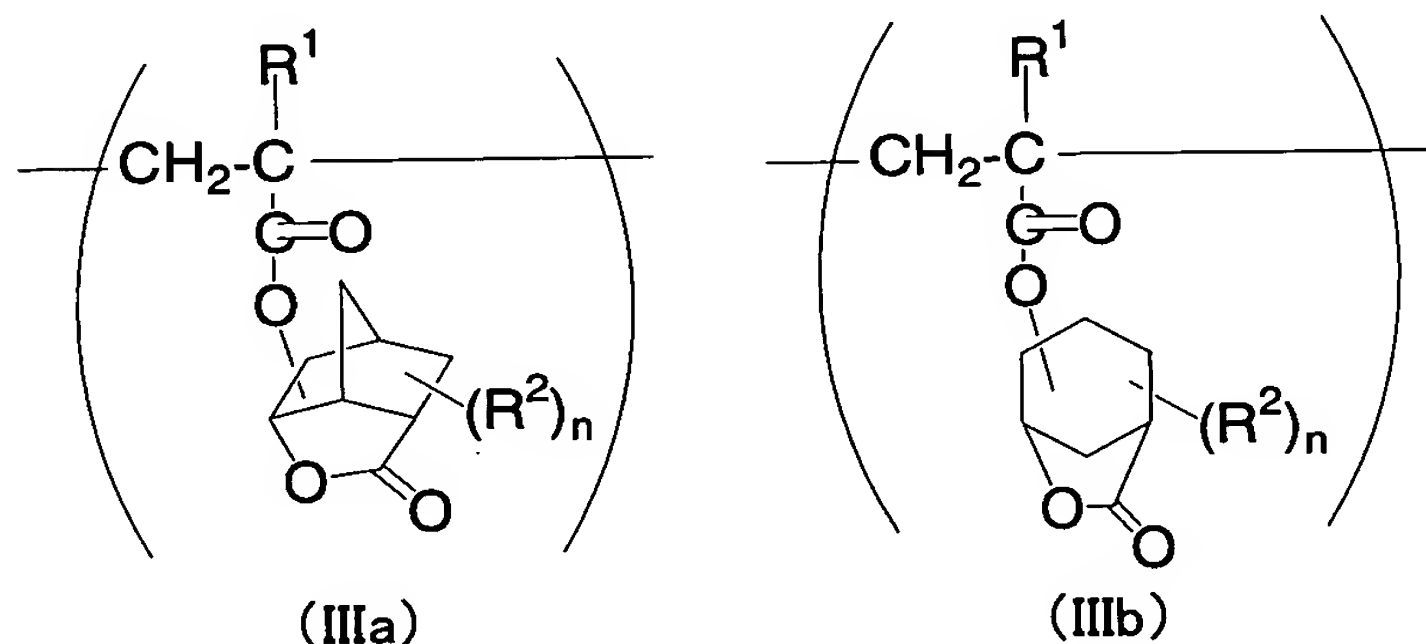
15 Though it is not preferred in the case of ArF exposure because of its large light absorption, there is no problem on light absorption in the case of KrF exposure and a structural unit of hydroxystyrene can be further contained.

[0040]

Particularly, to contain, in addition to the structural unit having an
20 acid-labile group, further at least one structural unit selected from the group consisting of a structural unit derived from p-hydroxystyrene, a structural unit derived from m-hydroxystyrene, a structural unit derived from 3-hydroxy-1-adamantyl (meth)acrylate, a structural unit derived from 3,5-dihydroxy-1-adamantyl (meth)acrylate, a structural unit derived from

(meth)acryloyloxy- γ -butyrolactone having a lactone ring optionally substituted by alkyl, a structural unit of the following formula (IIIa) and a structural unit of the following formula (IIIb), in the resin in the present composition, is preferable from the standpoint of the adhesiveness of resist to a substrate.

5 [0041]



In the formulae (IIIa) and (IIIb), R^1 and R^2 each independently represent hydrogen, methyl, trifluoromethyl or halogen, and n represents an integer of 1 to 3.

10 [0042]

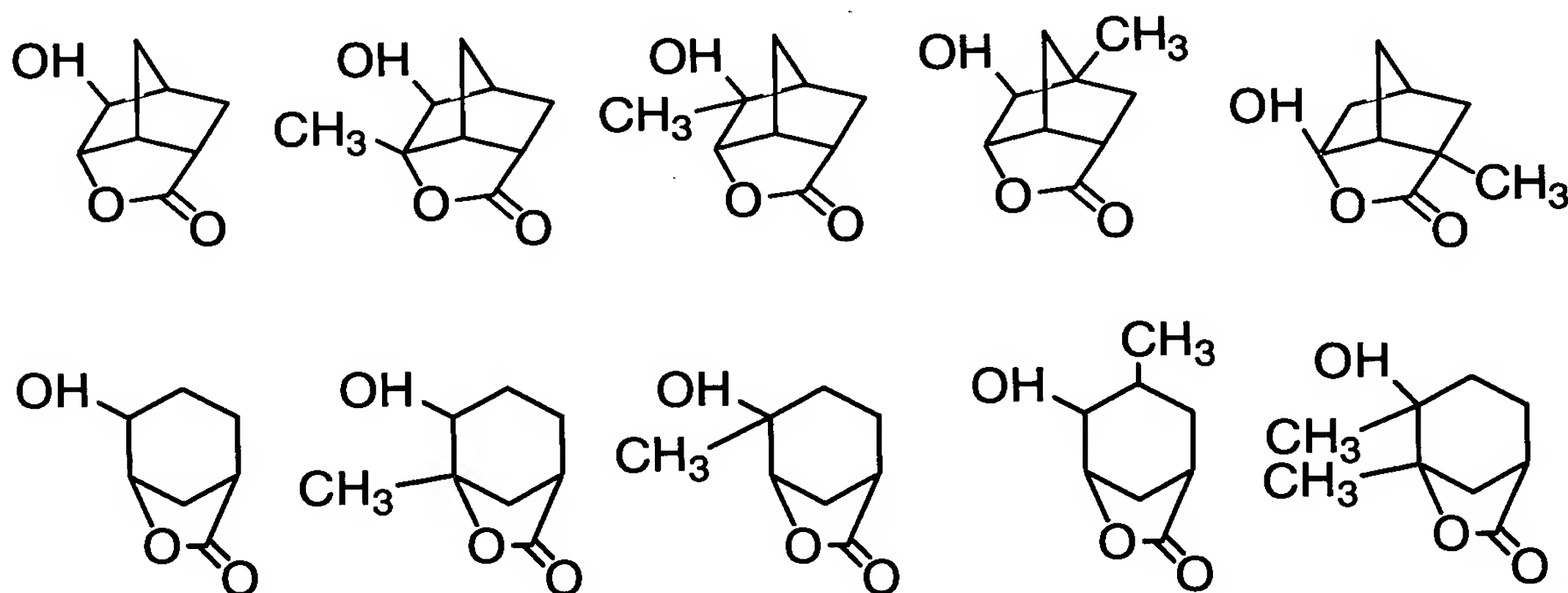
3-Hydroxy-1-adamantyl (meth)acrylate and 3,5-dihydroxy-1-adamantyl (meth)acrylate can be produced by, for example, reacting corresponding hydroxyadamantane with (meth)acrylic acid or its acid halide, and they are also commercially available.

15 Further, (meth)acryloyloxy- γ -butyrolactone can be produced by reacting α - or β -bromo- γ -butyrolactone having a lactone ring optionally substituted by alkyl with acrylic acid or methacrylic acid, or reacting α - or β -bromo- γ -butyrolactone having a lactone ring optionally substituted by alkyl with acrylic halide or methacrylic halide.

As monomers leading to structural units of the formulae (IIIa) and (IIIb), specifically listed are, for example, (meth)acrylates of alicyclic lactones having hydroxyl described below, and mixtures thereof, and the like. These esters can be produced, for example, by reacting corresponding alicyclic lactone having

5 hydroxyl with (meth)acrylic acids, and the production method thereof is described in, for example, JP2000-26446-A.

[0043]



10 [0044]

When any of the structural unit derived from 3-hydroxy-1-adamantyl (meth)acrylate, the structural unit derived from 3,5-dihydroxy-1-adamantyl (meth)acrylate, the structural unit derived from α -(meth)acryloyloxy- γ -butyrolactone, the structural unit derived from β -(meth)acryloyloxy- γ -butyrolactone and the structural unit of the formulae (IIIa) and (IIIb) is

15 contained in the resin, not only the adhesiveness of the resist to a substrate is improved, but also the resolution of the resist is improved.

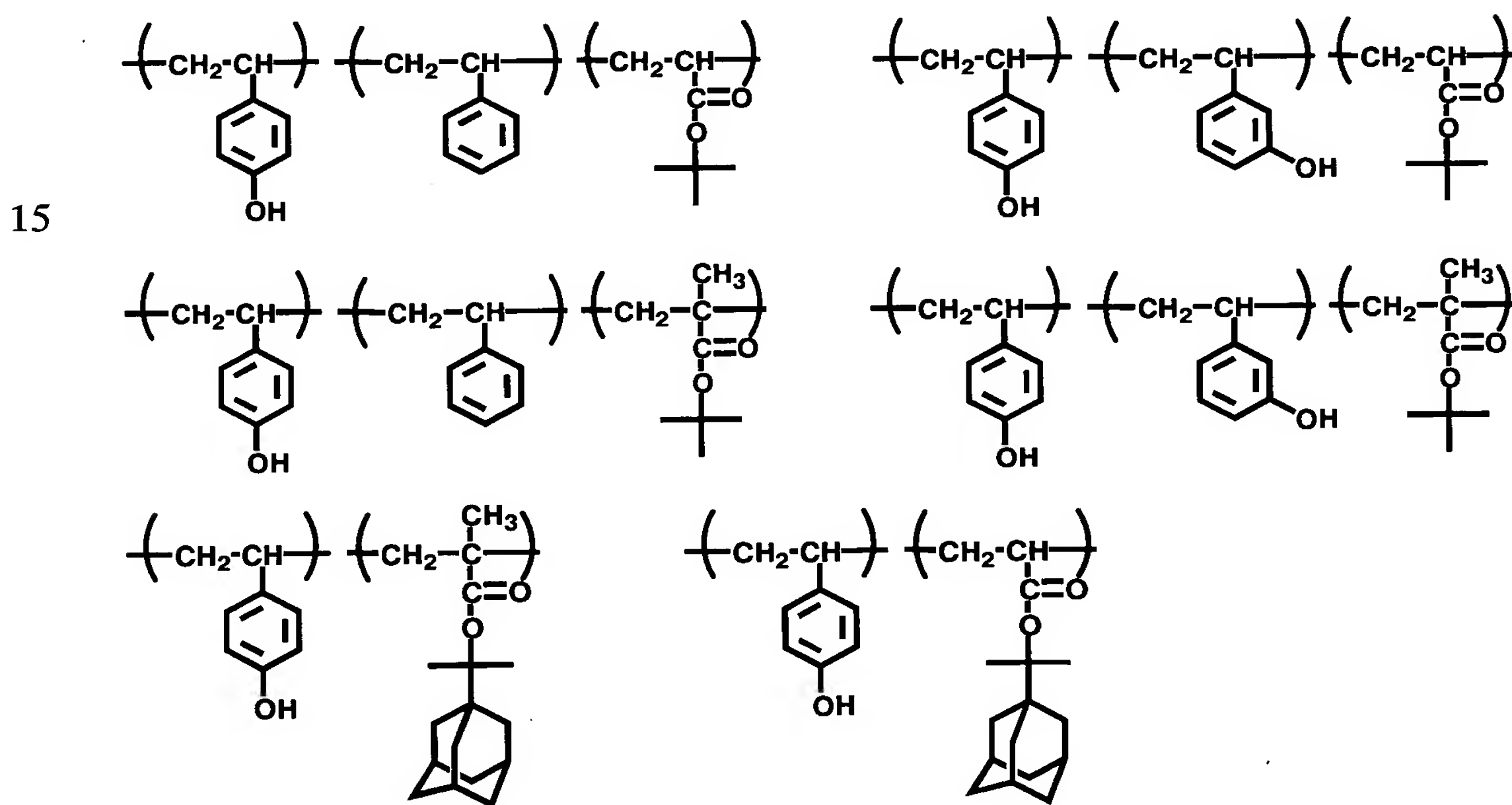
[0045]

Here, examples of the (meth)acryloyloxy- γ -butyrolactone include α

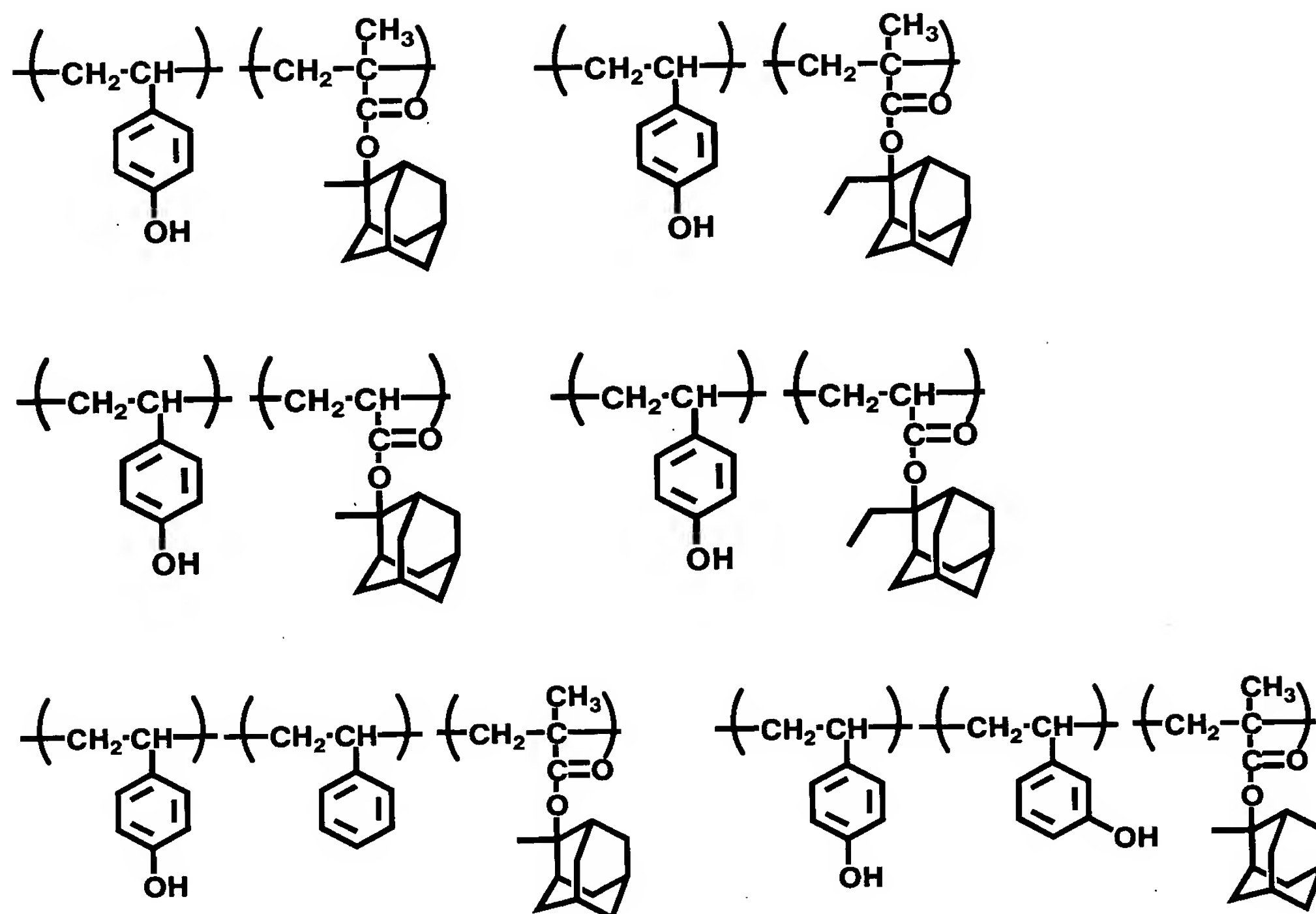
- acryloyloxy- γ -butyrolactone, α -methacryloyloxy- γ -butyrolactone, α -acryloyloxy- β , β -dimethyl- γ -butyrolactone, α -methacryloyloxy- β , β -dimethyl- γ -butyrolactone, α -acryloyloxy- α -methyl- γ -butyrolactone, α -methacryloyloxy- α -methyl- γ -butyrolactone, β -acryloyloxy- γ -butyrolactone, β -methacryloyloxy- γ -butyrolactone, β -methacryloyloxy- α -methyl- γ -butyrolactone and the like.

In the case of KrF excimer laser exposure, sufficient transmittance can be obtained even the structural unit derived from hydroxystyrene is contained in the resin. Specifically, copolymerization resins containing a structural unit derived from p- or m-hydroxystyrene as described below are listed. For obtaining such copolymerization resins, the corresponding (meth)acrylic ester monomer can be radical-polymerized with acetoxystyrene and styrene, and then the reaction mixture can be de-acetylated with an acid.

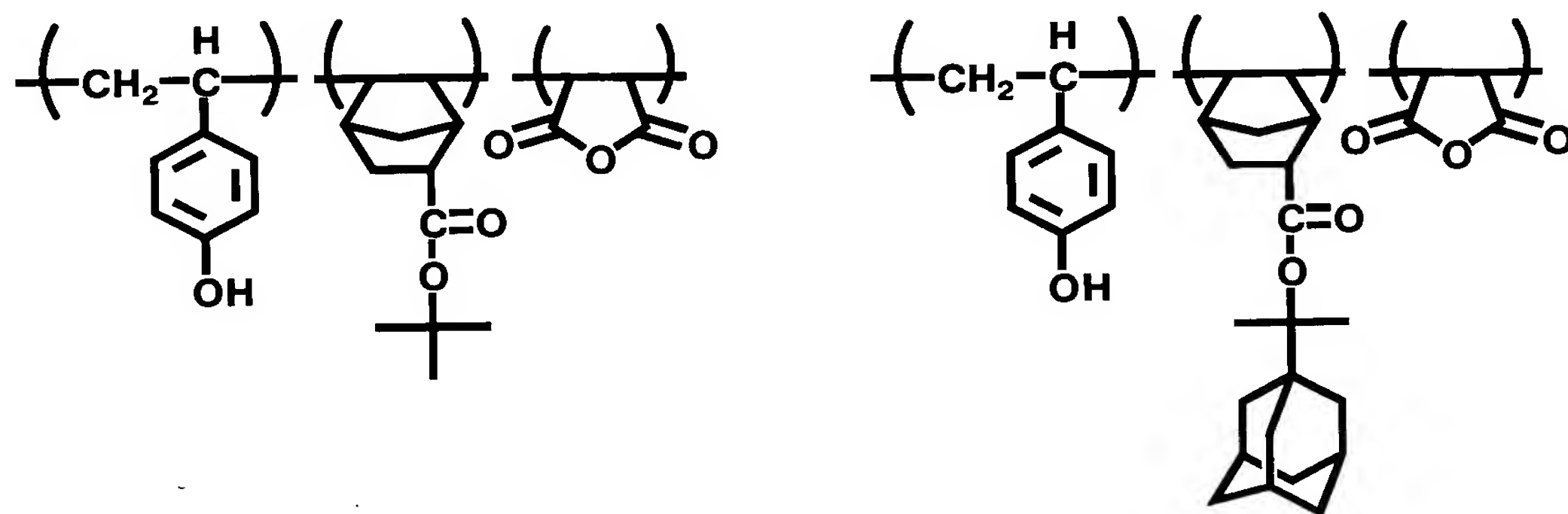
[0047]

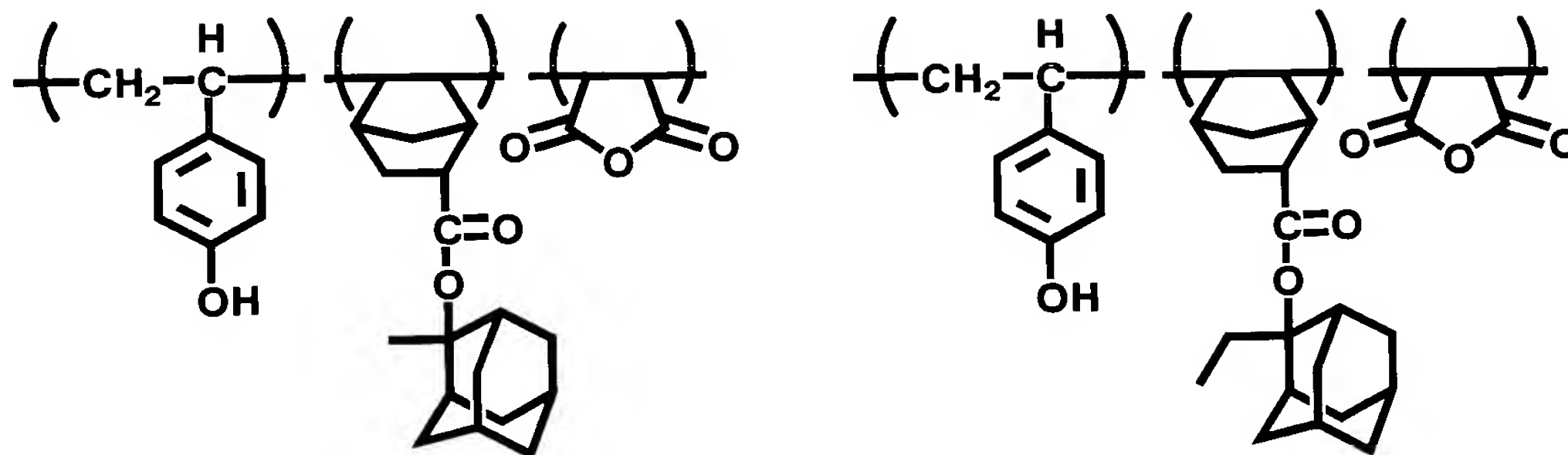


[0048]



5 [0049]





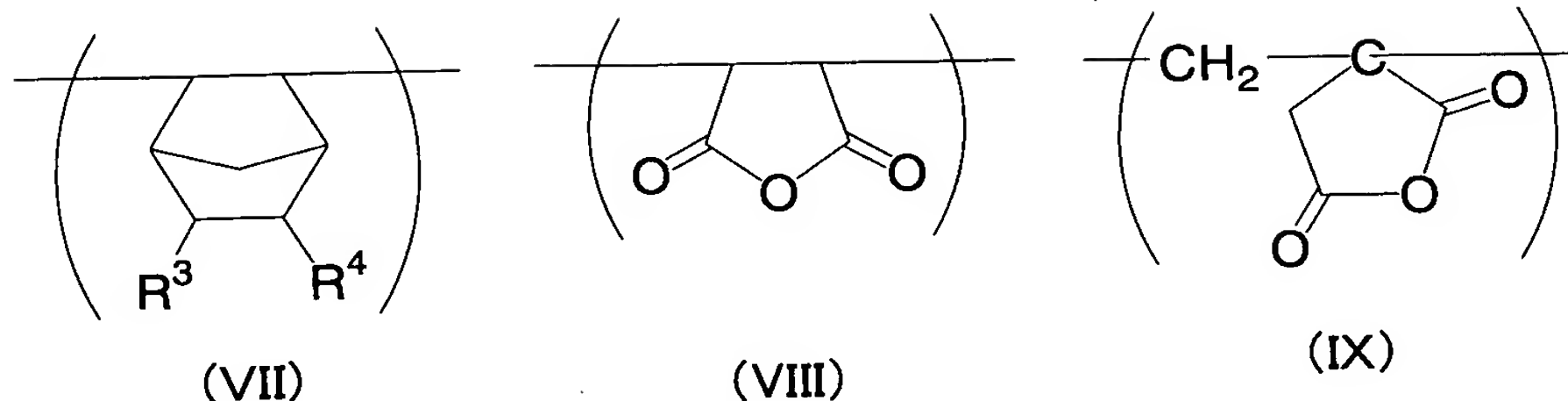
[0050]

In these cases, it is advantageous from the standpoint of dry etching resistance to contain 2-alkyl-2-adamantyl or 1-(1-adamantyl)-1-alkylalkyl as the acid labile group in the resin.

[0051]

The resin containing a structural unit derived from 2-norbornene shows strong structure because of alicyclic group directly present on its main chain and shows a property that dry etching resistance is excellent. The structural unit derived from 2-norbornene can be introduced into the main chain by radical polymerization using, for example, in addition to corresponding 2-norbornene, aliphatic unsaturated dicarboxylic anhydrides such as maleic anhydride and itaconic anhydride together. The structural unit derived from 2-norbornene is formed by opening of its double bond, and can be represented by the formula (VII). The structural unit derived from maleic anhydride and the structural unit derived from itaconic anhydride which are the structural unit derived from aliphatic unsaturated dicarboxylic anhydrides are formed by opening of their double bonds, and can be represented by the formula (VIII) and the formula (IX), respectively.

[0052]



[0053]

Here, R^3 and R^4 in the formula (VII) each independently represent
 5 hydrogen, alkyl having 1 to 3 carbon atoms, hydroxyalkyl having 1 to 3 carbon
 atoms, carboxyl, cyano or $-COOZ$ group in which Z represents alcohol residue,
 or R^3 and R^4 can bond together to form a carboxylic anhydride residue
 represented by $-C(=O)OC(=O)-$.

In R^3 and/or R^4 , examples of the alkyl include methyl, ethyl, propyl and
 10 isopropyl, specific examples of hydroxyalkyl include hydroxymethyl,
 2-hydroxyethyl and the like.

In R^3 and/or R^4 , $-COOZ$ group is an ester formed from carboxyl, and as
 the alcohol residue corresponding to Z, for example, optionally substituted
 alkyls having about 1 to 8 carbon atoms, 2-oxoxolan-3- or -4-yl and the like are
 15 listed, and as the substituent on the alkyl, hydroxyl, alicyclic hydrocarbon
 residues and the like are listed.

Specific examples of $-COOZ$ include methoxycarbonyl, ethoxycarbonyl,
 2-hydroxyethoxycarbonyl, tert-butoxycarbonyl, 2-oxoxalan-3-yloxycarbonyl,
 2-oxoxalan-4-yloxycarbonyl, 1,1,2-trimethylpropoxycarbonyl,
 20 1-cyclohexyl-1-methylethoxycarbonyl,
 1-(4-methylcyclohexyl)-1-methylethoxycarbonyl,

1-(1-adamantyl)-1-methylethoxycarbonyl and the like.

[0054]

Specific examples of the monomer used to derive the structural unit represented by the formula (VII) may include the followings;

- 5 2-norbornene,
- 2-hydroxy-5-norbornene,
- 5-norbornen-2-carboxylic acid,
- methyl 5-norbornen-2-carboxylate,
- t-butyl 5-norbornen-2-carboxylate,
- 10 1-cyclohexyl-1-methylethyl 5-norbornen-2-carboxylate,
- 1-(4-methylcyclohexyl)-1-methylethyl 5-norbornen-2-carboxylate,
- 1-(4-hydroxycyclohexyl)-1-methylethyl 5-norbornen-2-carboxylate,
- 1-methyl-1-(4-oxocyclohexyl)ethyl 5-norbornen-2-carboxylate,
- 1-(1-adamantyl)-1-methylethyl 5-norbornen-2-carboxylate,
- 15 1-methylcyclohexyl 5-norbornen-2-carboxylate,
- 2-methyl-2-adamantyl 5-norbornen-2-carboxylate,
- 2-ethyl-2-adamantyl 5-norbornen-2-carboxylate,
- 2-hydroxyethyl 5-norbornen-2-carboxylate,
- 5-norbornen-2-methanol,
- 20 5-norbornen-2, 3-dicarboxylic acid anhydride, and the like.

[0056]

The resin used in the present composition preferably contains structural unit(s) having an acid-labile group generally in a ratio of 10 to 80% by mol in all structural units of the resin though the ratio varies depending on the kind of

radiation for patterning exposure, the kind of an acid-labile group, and the like.

When the structural units particularly derived from 2-alkyl-2-adamantyl (meth)acrylate or 1-(1-adamantyl)-1-alkylalkyl (meth)acrylate are used as the acid-labile group, it is advantageous that the ratio of the structural units is 15%
 5 by mol or more in all structural units of the resin.

When, in addition to structural units having an acid-labile group, other structural units not easily dissociated by the action of an acid, for example, a structural unit derived from 3-hydroxy-1-adamantyl (meth)acrylate, a structural units derived from 3,5-dihydroxy-1-adamantyl (meth)acrylate or α
 10 -(meth)acryloyloxy- γ -butyrolactone, a structural units derived from β -(meth)acryloyloxy- γ -butyrolactone, a structural unit of the formula (IIIa) or (IIIb), a structural unit derived from hydroxystyrene, a structural unit of the formula (VII), a structural unit derived from maleic anhydride of the formula (VIII) which is a structural unit derived from an aliphatic unsaturated
 15 dicarboxylic anhydride, a structural unit derived from itaconic anhydride of the formula (IX) and the like are contained, it is preferable that the sum of these structural units is in the range of 20 to 90% by mol based on all structural units of the resin.

[0057]

20 When 2-norbornenes and aliphatic unsaturated dicarboxylic anhydride are used as copolymerization monomer, it is preferable to use them in excess amount in view of a tendency that these are not easily polymerized.

[0058]

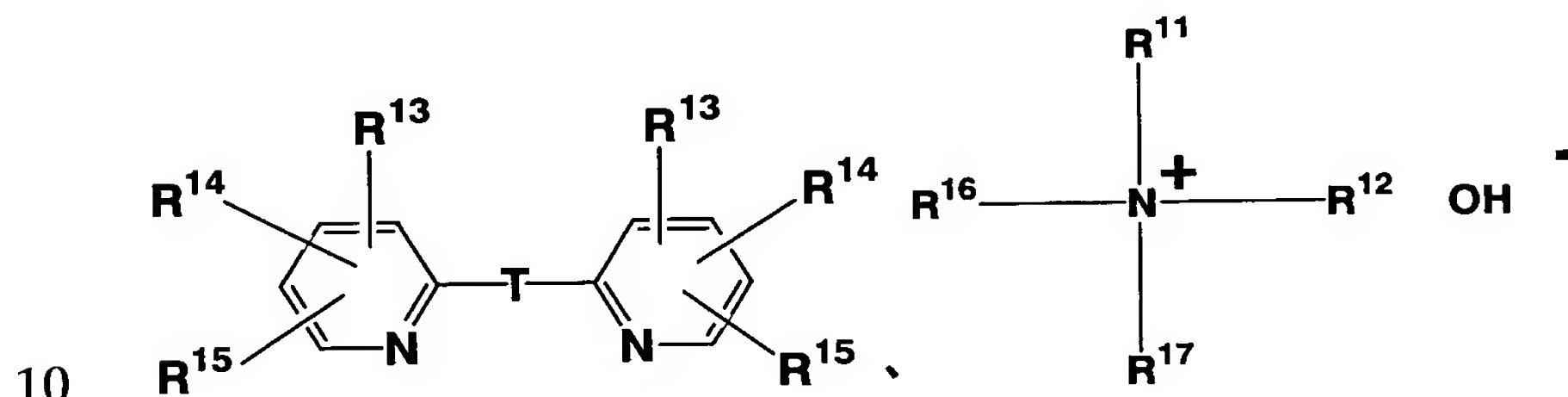
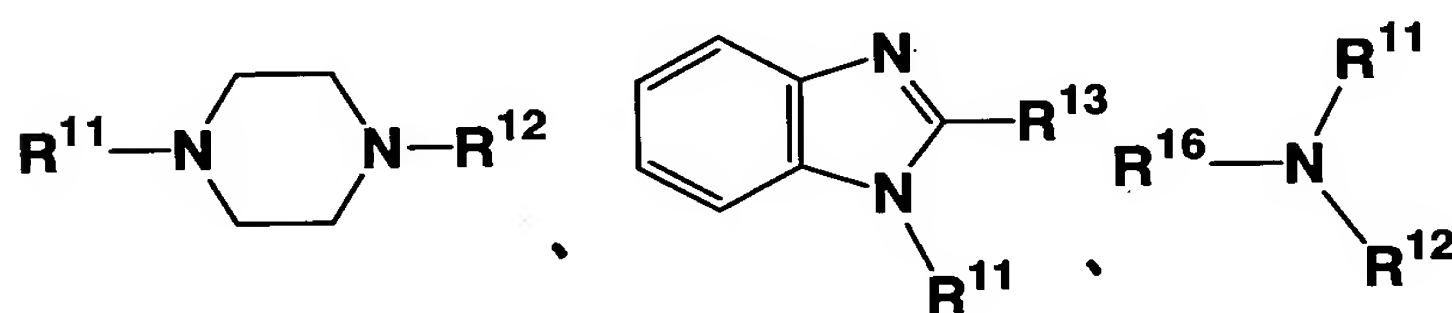
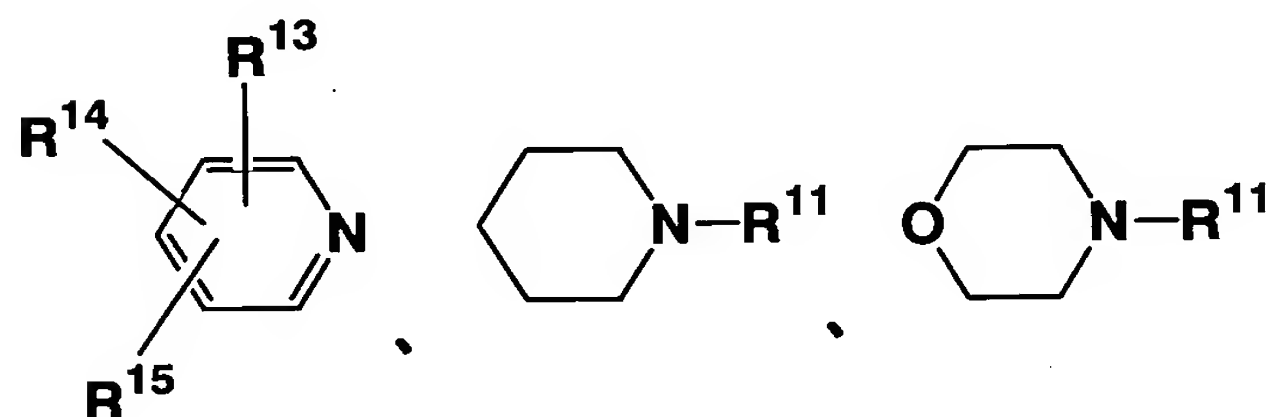
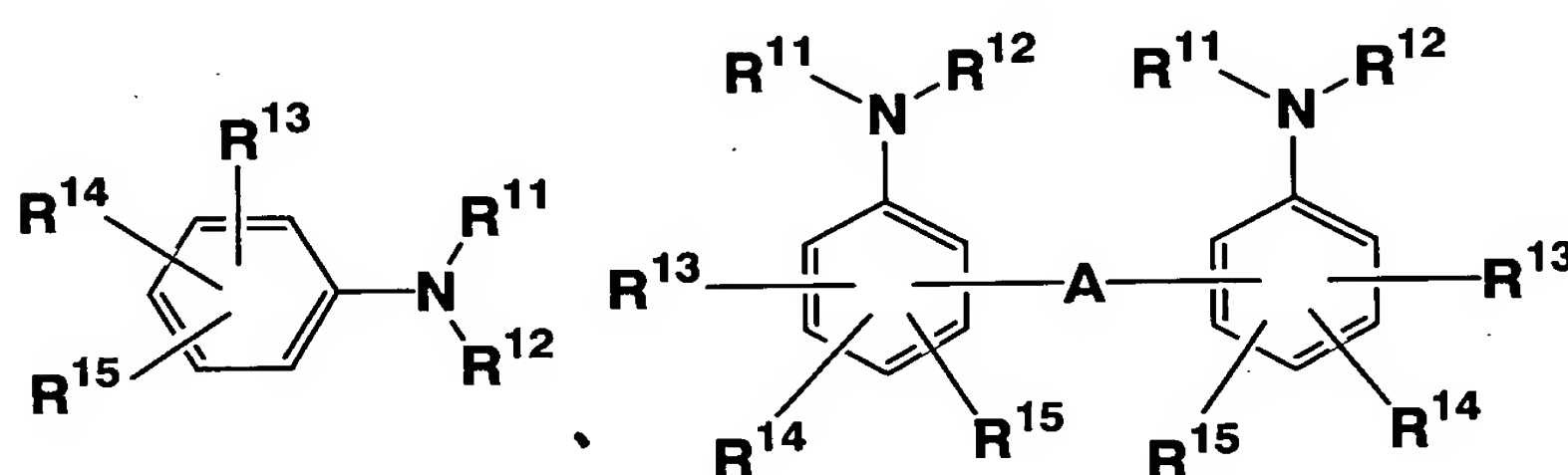
In the present composition, performance deterioration caused by

inactivation of acid which occurs due to post exposure delay can be diminished by adding basic compounds, particularly, basic nitrogen-containing organic compounds, for example, amines as a quencher.

Specific examples of such basic compounds include the ones

5 represented by the following formulae:

[0058]



[0060]

Wherein R^{11} , R^{12} and R^{17} each independently represent hydrogen, alkyl, cycloalkyl or aryl. The alkyl, cycloalkyl or aryl may each independently be

substituted by hydroxyl, amino, or alkoxy having 1 to 6 carbon atoms. The amino may be substituted by alkyl having 1 to 4 carbon atoms. The alkyl preferably has about 1 to 6 carbon atoms, the cycloalkyl preferably has about 5 to 10 carbon atoms, and the aryl preferably has about 6 to 10 carbon atoms.

5 R^{13} , R^{14} and R^{15} each independently represent hydrogen, alkyl, cycloalkyl, aryl or alkoxy. The alkyl, cycloalkyl, aryl or alkoxy may each independently be substituted by hydroxyl, amino, or alkoxy having 1 to 6 carbon atoms. The amino may be substituted by alkyl having 1 to 4 carbon atoms. The alkyl preferably has about 1 to 6 carbon atoms, the cycloalkyl preferably has
10 about 5 to 10 carbon atoms, the aryl preferably has about 6 to 10 carbon atoms, and the alkoxy preferably has about 1 to 6 carbon atoms.

R^{16} represents alkyl or cycloalkyl. The alkyl or cycloalkyl may each independently be substituted by hydroxyl, amino, or alkoxy having 1 to 6 carbon atoms. The amino may be substituted by alkyl having 1 to 4 carbon atoms. The
15 alkyl preferably has about 1 to 6 carbon atoms, and the cycloalkyl preferably has about 5 to 10 carbon atoms.

Z represents alkylene, carbonyl, imino, sulfide or disulfide. The alkylene preferably has about 2 to 6 carbon atoms.

Moreover, among $R^{11} - R^{17}$, in regard to those which can be
20 straight-chained or branched, either of these may be permitted.

[0061]

Examples of such compounds include hexylamine, heptylamine, octylamine, nonylamine, decylamine, aniline, 2-, 3- or 4-methylaniline, 4-nitroaniline, 1- or 2-naphtylamine, ethylenediamine, tetramethylenediamine,

- hexamethylenediamine, 4,4'-diamino-1,2-diphenylethane,
 4,4'-diamino-3,3'-dimethyldiphenylmethane,
 4,4'-diamino-3,3'-diethyldiphenylmethane, dibutylamine, dipentylamine,
 dihexylamine, diheptylamine, dioctylamine, dinonylamine, didecylamine,
 5 N-methylaniline, piperidine, diphenylamine, triethylamine, trimethylamine,
 tripropylamine, tributylamine, tripentylamine, trihexylamine, trihexylamine,
 triheptylamine, trioctylamine, trinonylamine, tridecylamine,
 methyldibutylamine, methyldipentylamine, methyldihexylamine,
 methyldicyclohexylamine, methyldiheptylamine, methyldioctylamine,
 10 methyldinonylamine, methyldidecylamine, ethyldibutylamine,
 ethyldipentylamine, ethyldihexylamine, ethyldiheptylamine, ethyldioctylamine,
 ethyldinonylamine, ethyldidecylamine, dicyclohexylmethanamine,
 tris[2-(2-methoxyethoxy)ethyl]amine, triisopropanolamine,
 N,N-dimethylaniline, 2,6-isopropylaniline, imidazole, pyridine,
 15 4-methylpyridine, 4-methylimidazole, bipyridine, 2,2'-dipyridylamine,
 di-2-pyridyl ketone, 1,2-di(2-pyridyl)ethane, 1,2-di(4-pyridyl)ethane,
 1,3-di(4-pyridyl)propane, 1,2-bis(2-pyridyl)ethylene,
 1,2-bis(4-pyridyl)ethylene, 1,2-bis(4-pyridyloxy)ethane, 4,4'-dipyridyl sulfide,
 4,4'-dipyridyl disulfide, 1,2-bis(4-pyridyl)ethylene, 2,2'-dipicolylamine,
 20 3,3'-dipicolylamine, tetramethylammonium hydroxide,
 tetraisopropylammonium hydroxide, tetrabutylammonium hydroxide,
 tetra-n-hexylammonium hydroxide, tetra-n-octylammonium hydroxide,
 phenyltrimethylammonium hydroxide,
 3-(trifluoromethyl)phenyltrimethylammonium hydroxide, choline, and the like.

[0062]

Furthermore, hindered amine compounds having piperidine skeleton as disclosed in JP-A-H11-52575 can be used as quencher.

[0063]

5 It is preferable that the present composition contains resin in an amount of about 80 to 99.9% by weight and the acid generator in an amount of 0.1 to 20% by weight based on the total solid content of the present composition.

 When basic compound is used as a quencher, it is preferable that the basic compound is contained in an amount of about 0.01 to 1% by weight based
10 on the total solid content of the present composition.

 The present composition can contain, if necessary, various additives in small amount such as a sensitizer, solution suppressing agent, other resins, surfactant, stabilizer, dye and the like.

[0064]

15 The present composition is usually in the form of a resist liquid composition in which the aforementioned ingredients are dissolved in a solvent, and the resist liquid composition is to be applied onto a substrate such as a silicon wafer by a conventional process such as spin coating. The solvent used here is sufficient to dissolve the aforementioned ingredients, have an adequate
20 drying rate, and give a uniform and smooth coat after evaporation of the solvent and, hence, solvents generally used in the art can be used.

 Examples thereof include glycol ether esters such as ethylcellosolve acetate, methylcellosolve acetate and propylene glycol monomethyl ether acetate; esters such as ethyl lactate, butyl lactate, amyl lactate and ethyl pyruvate

and the like; ketones such as acetone, methyl isobutyl ketone, 2-heptanone and cyclohexanone; cyclic esters such as γ -butyrolactone, and the like. These solvents can be used each alone or in combination of two or more.

[0065]

5 A resist film applied onto the substrate and then dried is subjected to exposure for patterning, then heat-treated for facilitating a deblocking reaction, and thereafter developed with an alkali developer. The alkali developer used here may be any one of various alkaline aqueous solutions used in the art, and generally, an aqueous solution of tetramethylammonium hydroxide or
10 (2-hydroxyethyl)trimethylammonium hydroxide (commonly known as “choline”) is often used.

Though the embodiments of the present invention are explained the above, it should be construed that embodiments disclosed here are examples in all aspects and not restrictive. It is intended that the scope of the present invention
15 is determined not by the above descriptions but by appended Claims, and includes all variations of the equivalent meanings and ranges to the Claims.

[0066]

The present invention will be described more specifically by way of examples, which are not construed to limit the scope of the present invention.
20 The “%” and “part(s)” used to represent the content of any component and the amount of any material used in the following examples are on a weight basis unless otherwise specifically noted. The weight-average molecular weight of any material used in the following examples is a value found by gel permeation chromatography using styrene as a standard reference material.

[0067]

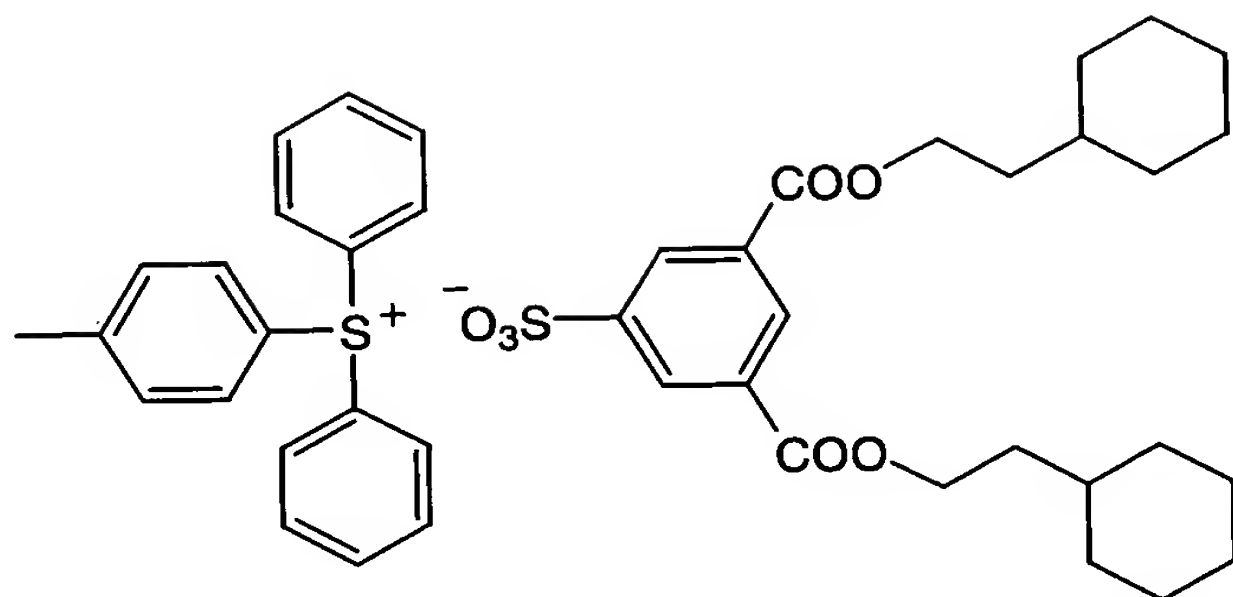
Acid generator synthesis example 1: Synthesis of acid generator B1

Into a flask was charged 6 parts of 5-sulfoisophtalic acid and 50 parts of cyclohexaneethanol, and the mixture was stirred at 135 to 140 °C for 9 hours.

- 5 After cooling, to this was added 50 parts of dimethylsulfoxide, 10 parts of methanol and 200 parts of n-heptane, the mixture was stirred and settled to give two separate layers. After separating the bottom layer from the upper layer, the bottom layer was washed with n-heptane twice. The mixture obtained by correcting the upper layer and two washed n-heptane was concentrated by
- 10 evaporating n-heptane and methanol. To the solution obtained was added 3.0 parts of silver oxide, and the mixture was stirred for 16 hours at room temperature. After filtration, to the filtrate was added dropwise the mixed solution of 8.67 parts of p-tolyldiphenylsulfonium iodide and 86.7 parts of methanol, and then the mixture was stirred for 16 hours at room temperature.
- 15 After filtration, to the filtrate was 200 parts of ethyl acetate, and washed with 100 parts of water 5 times. The organic layer obtained was concentrated. The concentrate was washed with 200 parts of n-heptane and then concentrated, and the washing and concentration was repeated twice. The concentrate was washed with another 200 parts of n-heptane and then washed, concentrated and filtrated
- 20 to obtain 6.24 parts of pale yellow crystals.

It was confirmed that the structure of the crystals was the following formula by NMR ("GX-270" manufactured by JEOL Ltd.) and mass spectrometry (LC analyser is No.1100 manufactured by HP, MASS analyser is LC/MSD manufactured by HP).

[0068]



[0069]

$^1\text{H-NMR}$ (chloroform-d, internal standard substance: tetramethylsilane):

5 δ (ppm)

0.94-1.00 (m, 4H); 1.14-1.26 (m, 6H); 1.41-1.44 (m, 2H); 1.62-1.76 (m, 14H);

2.44 (s, 3H); 4.33 (t, 4H); 7.46 (d, 2H) ; 7.65 – 7.77 (m, 12H) ; 8.61 (s, 1H) ;

8.77 (d, 2H)

MS (ESI (+) Spectrum): M^+ 277.2

10 MS (ESI (-) Spectrum): M^- 465.2

[0070]

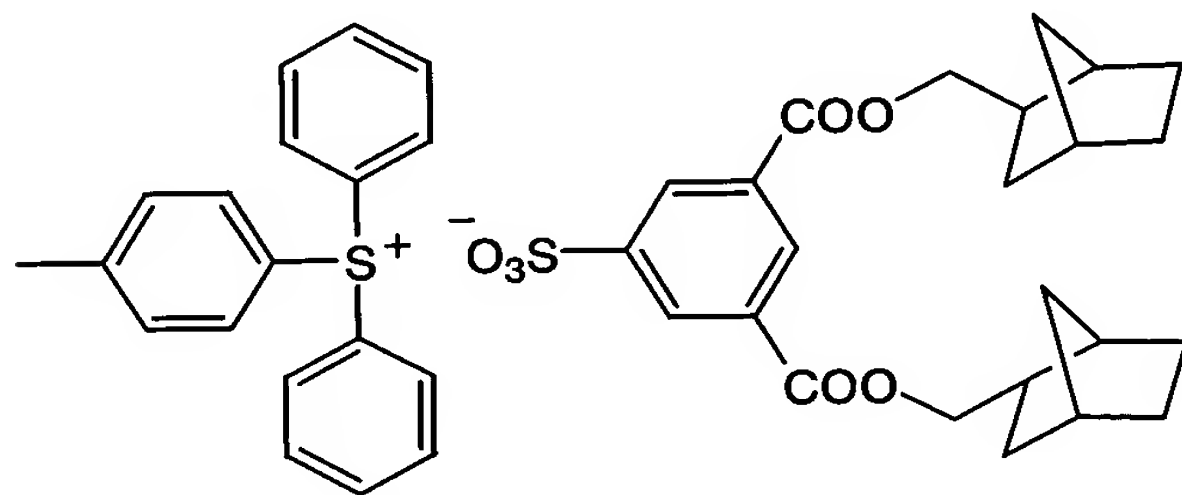
Acid generator synthesis example 2: Synthesis of acid generator B2

Into a flask was charged 20.0 parts of 5-sulfoisophthalic acid, 18.0 parts of 2-norbornanemethanol and 80.0 parts of toluene, and the mixture was refluxed while dehydration for 4 hours. After cooling, the reaction mixture was charged to 500 parts of n-heptane, and then stirred at for an hour. The resulting mixture was filtrated and the solid obtained was dried under reduced pressure to obtain 24.4 parts of diester. 15 parts of the diester was dissolved in 150 parts of methanol, and to the solution was added 4.5 parts of silver oxide, and the mixture was stirred for 12 hours at room temperature. After filtration, to the filtrate was

added dropwise the mixed solution of 13.1 parts of p-tolyldiphenylsulfonium iodide and 131 parts of methanol, and then the mixture was stirred for 12 hours at room temperature. After filtration, to the filtrate was 200 parts of ethyl acetate, and washed with 100 parts of water 5 times. The organic layer obtained was
 5 filtrated and then concentrated. The concentrate was washed with 300 parts of n-heptane and then concentrated, and the washing and concentration was repeated seven times. The concentrate was washed with another 300 parts of n-heptane and then washed, concentrated completely to obtain 15.0 parts of brown crystals.

10 It was confirmed that the structure of the crystals was the following formula by mass spectrometry (LC analyser is No.1100 manufactured by HP, MASS analyser is LC/MSD manufactured by HP).

[0071]



15

[0072]

MS (ESI (+) Spectrum): M+ 277.2

MS (ESI (-) Spectrum): M- 461.2

[0073]

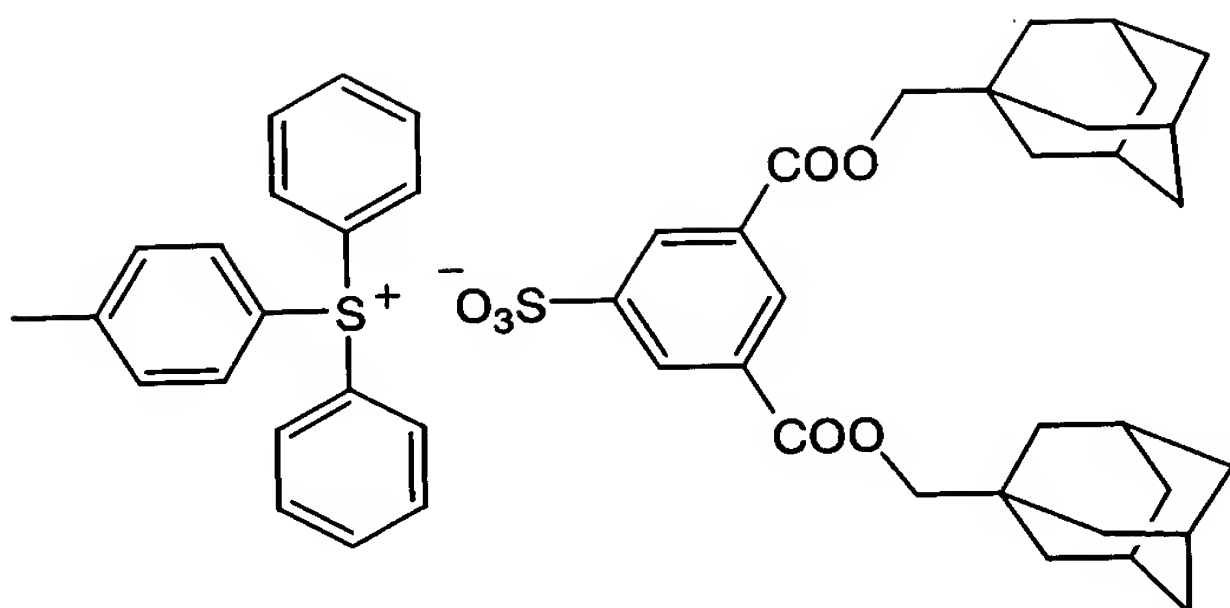
20 Acid generator synthesis example 3: Synthesis of acid generator B3

After charging 30.0 parts of 1-adamantanemethanol and 180 parts of

toluene into a flask, the mixture was heated to 80 °C. To this was added 5-sulfoisophthalic acid, and the mixture was refluxed while dehydration for 6 hours. After cooling, the reaction mixture was charged to 1000 parts of n-heptane, and then stirred at for an hour. The resulting mixture was filtrated and the solid obtained was dried under reduced pressure to obtain 40.0 parts of diester. 39.0 parts of the diester was dissolved in 234 parts of methanol, and to the solution was added 12.5 parts of silver oxide, and the mixture was stirred for 12 hours at room temperature. After filtration, to the filtrate were added 95.0 parts of methanol and 190 parts of chloroform, and further added dropwise the mixed solution of 23.7 parts of p-tolyldiphenylsulfonium iodide and 237 parts of methanol, and then the mixture was stirred for 12 hours at room temperature. After filtration, to the filtrate was 500 parts of ethyl acetate, and washed with 125 parts of water thrice. The organic layer obtained was filtrated and then concentrated. The concentrate was washed with 300 parts of n-heptane and then concentrated, and the washing and concentration was repeated seven times. The concentrate was washed with another 300 parts of n-heptane and then washed, concentrated completely to obtain 35.7 parts of white crystals.

It was confirmed that the structure of the crystals was the following formula by NMR (“GX-270” manufactured by JEOL Ltd.) and mass spectrometry (LC analyser is No.1100 manufactured by HP, MASS analyser is LC/MSD manufactured by HP).

[0074]



[0075]

$^1\text{H-NMR}$ (chloroform-d, internal standard substance: tetramethylsilane):

δ (ppm)

5 1.62-1.75 (m, 24H); 1.98 (brs, 6H); 2.44 (s, 3H); 3.93 (s, 4H); 7.46 (d, 2H) ; 7.64
 -7.80 (m, 12H) ; 8.63 (t, 1H) ; 8.79 (d, 2H)

MS (ESI (+) Spectrum): M^+ 277.2

MS (ESI (-) Spectrum): M^- 541.2

[0076]

10 Intermediate for acid generator synthesis example

(1) After charging 50 parts of 4-chloro-3,5-dinitrobenzoic acid, 0.3 part of 98% sulfuric acid, 78 parts of cyclohexylethanol and 50 parts of sulfolane into a flask, the mixture was heated to 100 to 110 °C, and was maintained at the same temperature for 8 to 10 hours. After checking the disappearance of

15 4-chloro-3,5-dinitrobenzoic acid by HPLC, the reaction mass was cooled to room temperature under atmospheric pressure, and to the mass was 240 parts of methanol, and was stirred for 30 minutes. The resulting mixture was filtrated to obtain crystals, and the crystals were washed with 40 parts of methanol and then dried to obtain 58 parts of 2-cyclohexylethyl 4-chloro-3,5-dinitrobenzoate

20 (Purity: 98%, Yield: 81%).

(2) 50 parts of 2-cyclohexylethyl 4-chloro-3,5-dinitrobenzoate was dissolved in 157 parts of acetonitrile. To the solution was added dropwise the solution of 35.4 parts of sodium sulfite and 72 parts of water at room temperature. To the mixed solution 1965 parts of acetonitrile little by little, and then was added 500 parts of water to obtain uniform solution. The solution was heated to 80 °C and maintained the temperature with stirring for 3 hours. After checking the disappearance of 2-cyclohexylethyl 4-chloro-3,5-dinitrobenzoate by HPLC, the resulting solution was concentrated 80 °C under reduced pressure. To the concentrate was added 80 parts of methanol, and stirred for 30 minutes. The crystals precipitated were filtrated and washed with 40 parts of methanol, and the filtrate was concentrated at 80 °C to obtain yellow crystals. Further, to the crystals was added 400 ml of isopropanol and the mixture was subjected to azeotropic dehydration. The crystals were filtrated and washed with 200 ml of isopropanol, and dried to obtain 42.2 parts of sodium 4-(2-cyclohexylethoxycarbonyl)-2,6-dinitrobenzenesulfonate (Purity:90.7%, Yield:70%).

[0077]

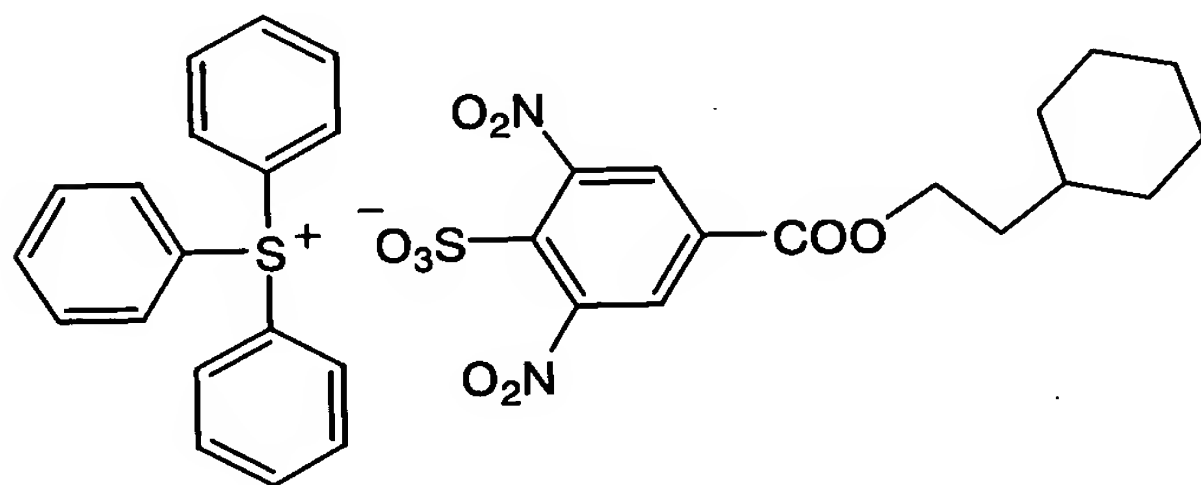
Acid generator synthesis example 4: Synthesis of acid generator B4

5.0 parts of sodium 4-(2-cyclohexylethoxycarbonyl)-2,6-dinitrobenzenesulfonate obtained in intermediate for acid generator synthesis example was dissolved in 50.0 parts of water, 50.0 parts of dimethylformamide and 50.0 parts of methanol. To the solution was added mixed solution of 3.5 parts of triphenylsulfonium chloride and 50.0 parts of water. After stirred for 12 hours, the reaction mixture was filtrated, and then the filtrate was concentrated.

The concentrate was dissolved in 200 parts of chloroform, the solution was washed with ion-exchanged water, and the organic layer obtained was concentrated. To the concentrate was added 50 parts of tert-butyl methyl ether and washed. The washed concentrate was filtrated and dried under reduced
 5 pressure to obtain 3.6 parts of white crystals.

It was confirmed that the structure of the crystals was the following formula by NMR ("GX-270" manufactured by JEOL Ltd.).

[0078]



10 [0079]

^1H -NMR (chloroform-d, internal standard substance: tetramethylsilane):

δ (ppm)

0.91-1.03 (m, 2H); 1.13-1.28 (m, 3H); 1.36-1.45 (m, 1H); 1.63-1.80 (m, 7H);
 4.40 (t, 2H); 7.62-7.78 (m, 15H); 8.17 (d, 2H)

15 [0080]

Acid generator synthesis example 5: Synthesis of acid generator B5

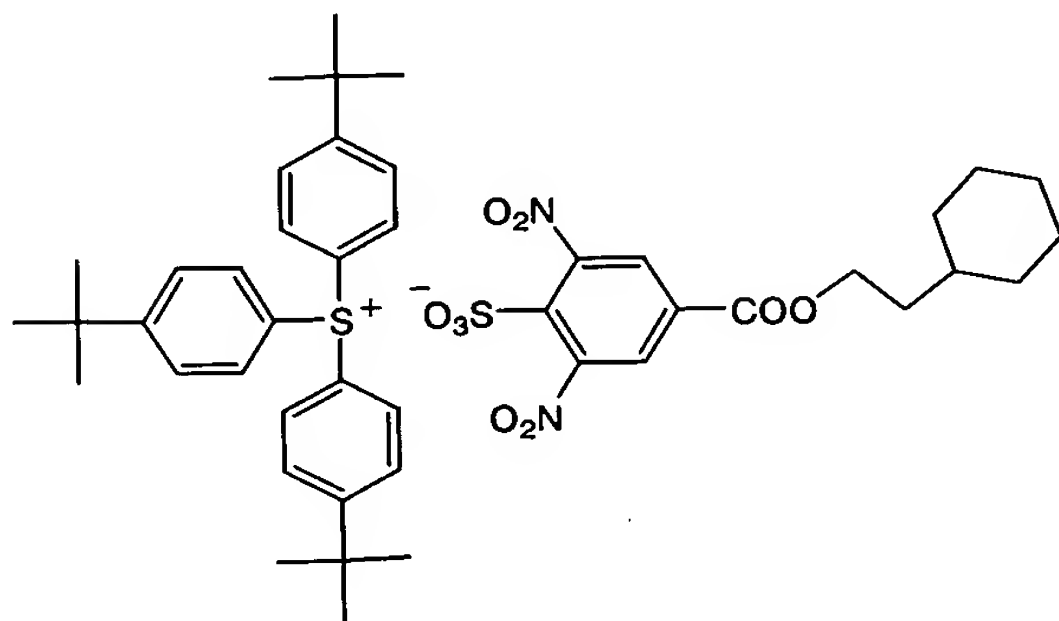
(1) 11.20 parts of sodium 4-(2-cyclohexylethoxycarbonyl)-2,6-dinitrobenzenesulfonate was dissolved in 60.0 parts of ion-exchanged water and 60 parts of methanol. The solution was passed thrice through a column filled
 20 with 32.07 parts of ion-exchange resin (Duolite C20 H type, manufactured by Sumitomo Chemical Co., Ltd.). After concentrating to eliminate methanol, the

concentrate was freeze-dried to obtain 9.87 parts of 2-cyclohexylethyl 4-sulfo-3,5-dinitrobenzoate.

(2) 3.00 parts of 2-cyclohexylethyl 4-sulfo-3,5-dinitrobenzoate, 50 parts of ion-exchanged water and 30 parts of methanol were charged into four-necked flask. To this was added 0.92 part of silver oxide and the mixture was stirred for 15 hours. After filtration, to the filtrate was added 4.17 parts of tris(4-tert-butylphenyl)sulfonium iodide and 42 parts of methanol, and the mixture was stirred for 15 hours. To the resulting mixture was added 200 parts of chloroform to extract. The mixture was shaken and then settled to give organic phase and aqueous phase. The aqueous phase was extracted with 50 parts of chloroform twice. The organic phases were combined and washed with 60 parts of ion-exchanged water thrice. The washed organic phase was concentrated, and then to the concentrate was added 100 parts of tert-butyl methyl ether to give precipitate. The precipitate was filtered and dried to obtain 5.26 parts of the object compound.

It was confirmed that the structure of the crystals was the following formula by NMR ("GX-270" manufactured by JEOL Ltd.).

[0081]



[0081]

¹H-NMR (chloroform-d, internal standard substance: tetramethylsilane):

δ (ppm)

0.87-0.99 (m, 2H) ; 1.09-1.42 (m, 33H) ; 1.55-1.73 (m, 5H) ; 4.37 (t, 2H) ;

5 7.77-7.85 (m, 12H) ; 8.35 (s, 2H)

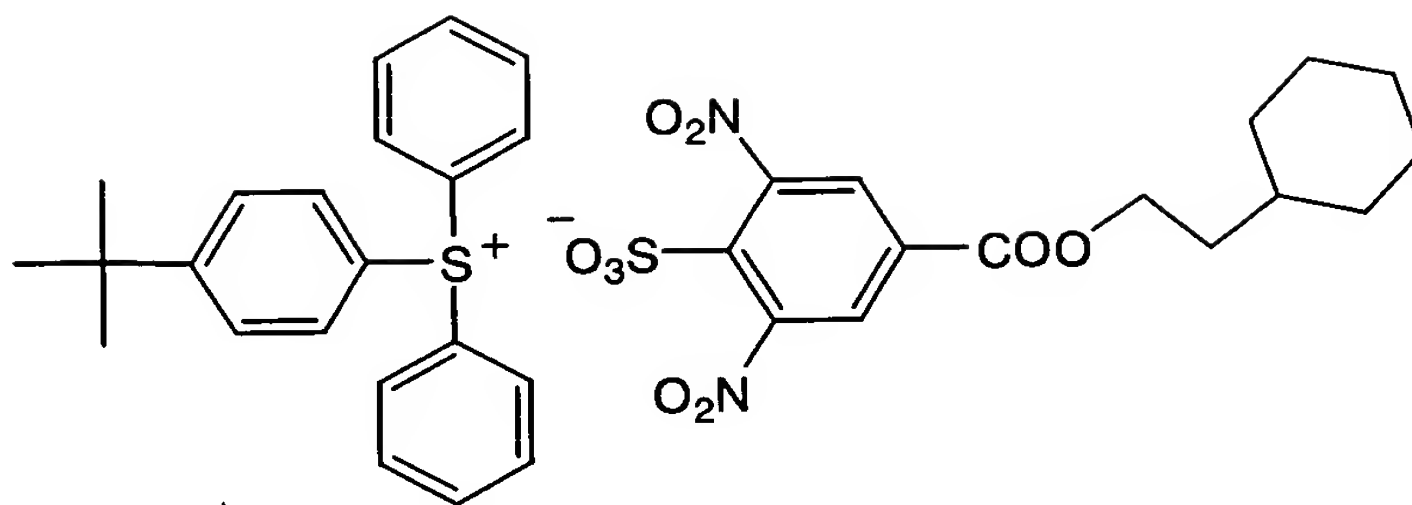
[0082]

Acid generator synthesis example 6: Synthesis of acid generator B6

3.50 parts of 2-cyclohexylethyl 4-sulfo-3,5-dinitrobenzoate, 50 parts of ion-exchanged water and 35 parts of methanol were charged into four-necked
10 flask. To this was added 1.07 part of silver oxide and the mixture was stirred for 15hours. After filtration, to the filtrate was added 3.88 parts of 4-tert-butylphenyldiphenylsulfonium iodide and 20 parts of methanol, and the mixture was stirred for 15 hours. To the resulting mixture was added 200 parts of chloroform to extract. The mixture was shaken and then settled to give
15 organic phase and aqueous phase. The aqueous phase was extracted with 50 parts of chloroform twice. The organic phases were combined and washed with 60 parts of ion-exchanged water thrice. The washed organic phase was concentrated, and then to the concentrate was added 100 parts of tert-butyl methyl ether to give precipitate. The precipitate was filtered and dried to obtain
20 4.81 parts of the object compound.

It was confirmed that the structure of the crystals was the following formula by NMR (“GX-270” manufactured by JEOL Ltd.).

[0084]



[0085]

$^1\text{H-NMR}$ (chloroform-d, internal standard substance: tetramethylsilane):

δ (ppm)

- 5 0.87-0.99 (m, 2H) ; 1.10-1.74 (m, 20H) ; 4.35 (t, 2H) ; 7.74-7.90 (m, 14H) ;
8.33 (s, 2H)

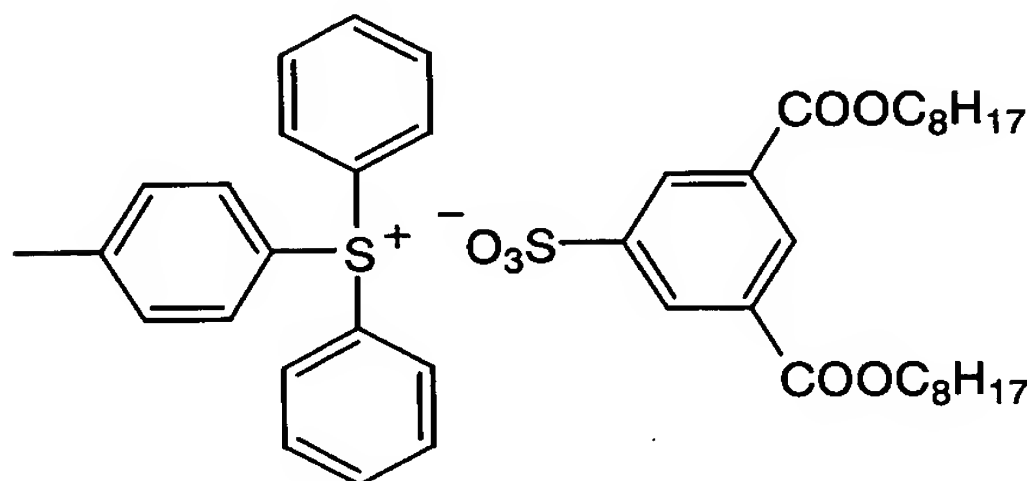
[0086]

Acid generator synthesis example 7: Synthesis of acid generator C1

- 10 The reactions and post treatments were conducted in the same manner as
in Acid generator synthesis example 1 except that n-octanol was used instead of
cyclohexaneethanol, and yellow oil product was obtained.

- It was confirmed that the structure of the oil product was the following
formula by NMR ("GX-270" manufactured by JEOL Ltd.) and mass
spectrometry (LC analyser is No.1100 manufactured by HP, MASS analyser is
15 LC/MSD manufactured by HP).

[0087]



[0088]

¹H-NMR (chloroform-d, internal standard substance: tetramethylsilane):

δ (ppm)

0.89 (t, 6H); 1.19-1.39 (m, 20H); 1.72(dd, 4H) ; 2.44 (s, 3H) ; 4.29 (t, 4H); 7.46
5 (d, 2H); 7.62—7.77 (m, 12H); 8.62 (s, 1H) ; 8.79 (d, 2H)

MS (ESI (+) Spectrum): M+ 277.2

MS (ESI (-) Spectrum): M- 469.2

[0089]

Resin synthesis example 1 (synthesis of resin A1)

10 2-Ethyl-2-adamantyl methacrylate,

5-methacryloyloxy-2,6-norbornenelactone and

α-methacryloyloxy-γ-butyrolactone were charged at a molar ratio of 35:40:25

(12.42 g:12.70 g:5.58 g), and equal weight amount (30.70 g) to all monomers of

1,4-dioxane was added, and then was added 3mol% (0.70 g) based on all

15 monomers of azobisisobutyronitrile as an initiator to prepare solution. In

another flask, one and a half times by weight (46.04 g) to all monomers of

1,4-dioxane was charged and heated to 87 °C. To this was added the solution

obtained above over one hour and the mixture was stirred for 5 hours

maintaining the temperature. Then, operation of pouring into large amount of

20 n-heptane to cause crystallization was repeated three times for purification, and

then dried to obtain 25.4 g (Yield: 82.7%) of copolymer having an average

molecular weight of 8900. This is called resin A1.

[0090]

Resin synthesis example 2 (synthesis of resin A2)

2-Ethyl-2-adamantyl methacrylate, 3-hydroxy-1-adamantyl
methacrylate and α -methacryloyloxy- γ -butyrolactone were charged at a molar
ratio of 5:2.5:2.5 (20.0 parts:9.5 parts:7.3 parts), and methyl isobutyl ketone in
twice weight based on all monomers was added, to prepare solution. To the
5 solution was added azobisisobutyronitrile as an initiator in a ratio of 2 mol%
based on all monomers molar amount, and the mixture was heated at 80 °C for
about 8 hours. Then, the reaction solution was poured into large amount of
heptane to cause precipitation, and this operation was repeated three times for
purification. As a result, copolymer having a weight-average molecular weight
10 of about 9,200 was obtained. This is called resin A2.

[0091]

As Resin A3, IHM-55-10K(Trade No., the product of Mitsubishi Rayon
Co., Ltd.) was used.

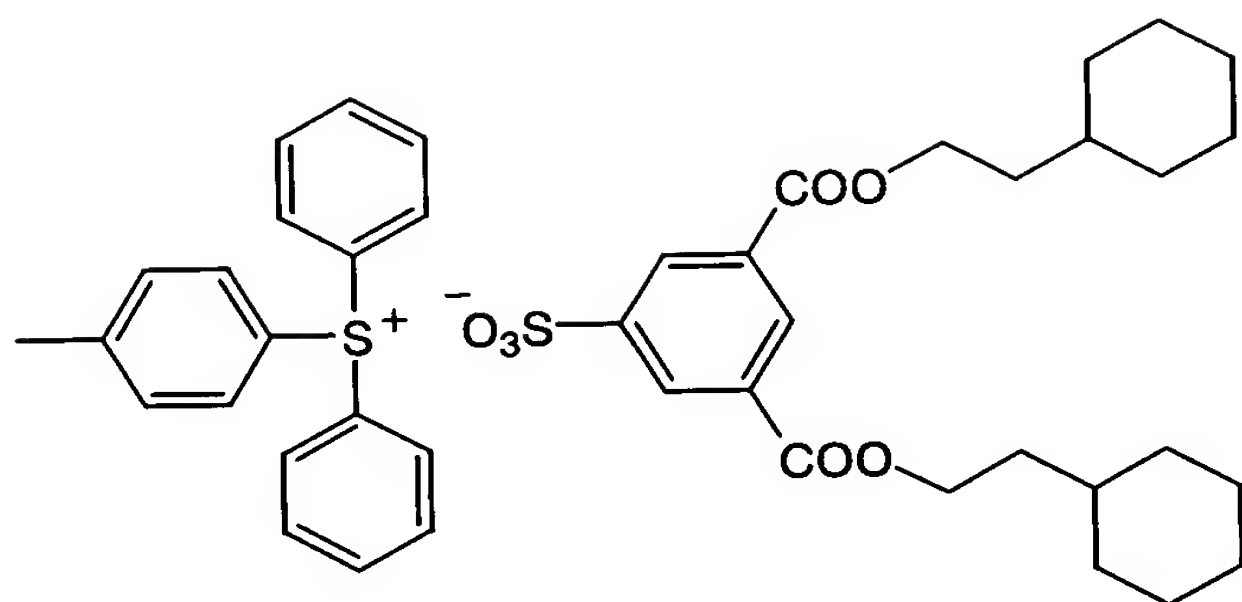
[0092]

15 Next, resist compositions were prepared by mixing raw materials shown
below in addition to the resins obtained in the above-mentioned resins, and
filtrating through a fluorine resin filter having pore diameter of 0.2 μ m.

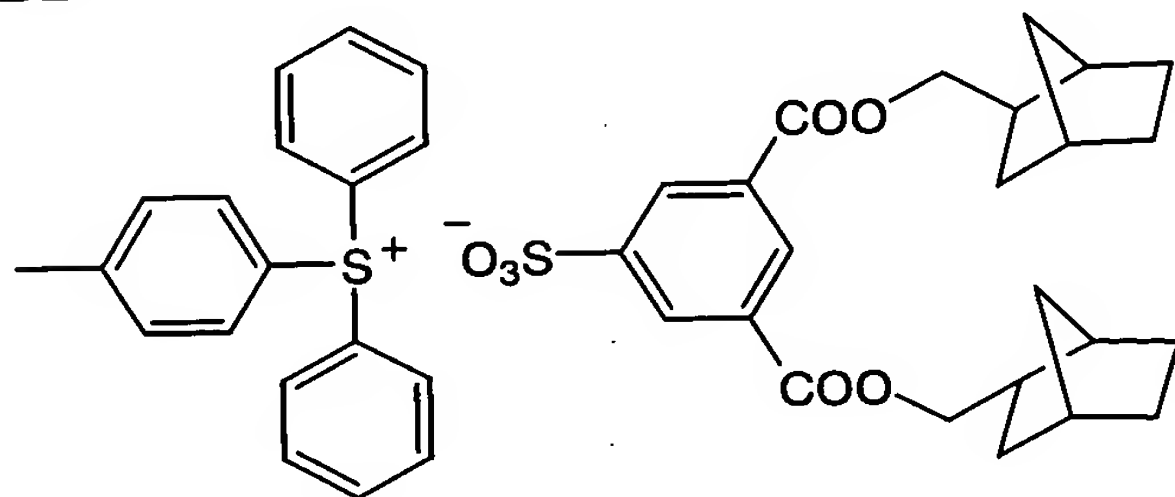
[0093]

<Acid generator>

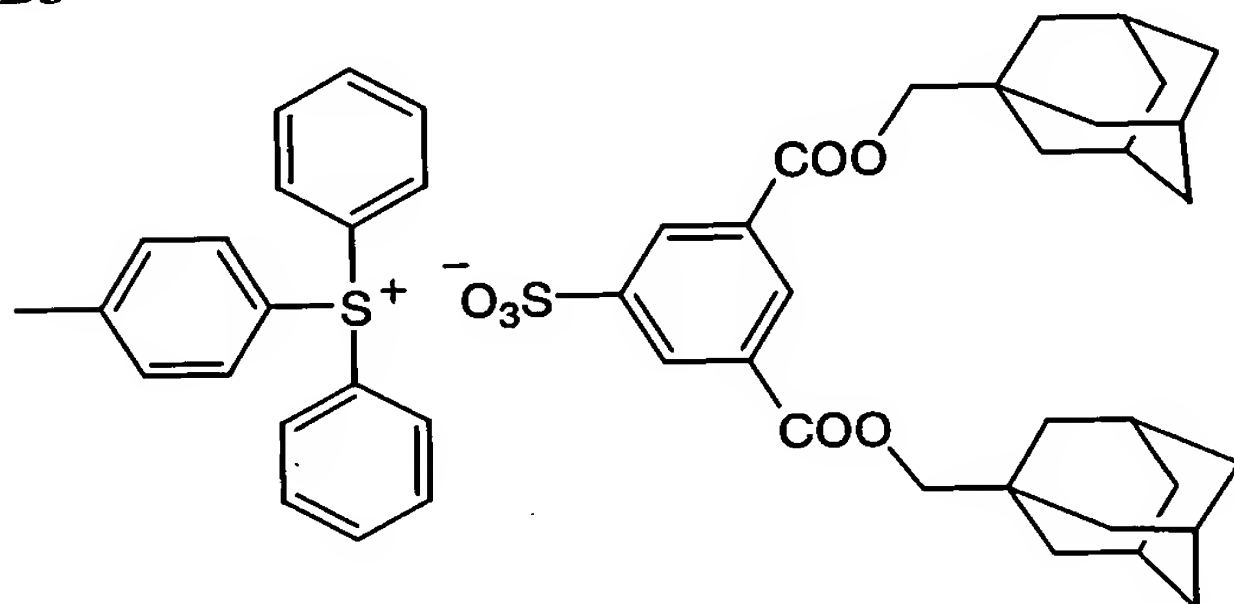
20 B1 :



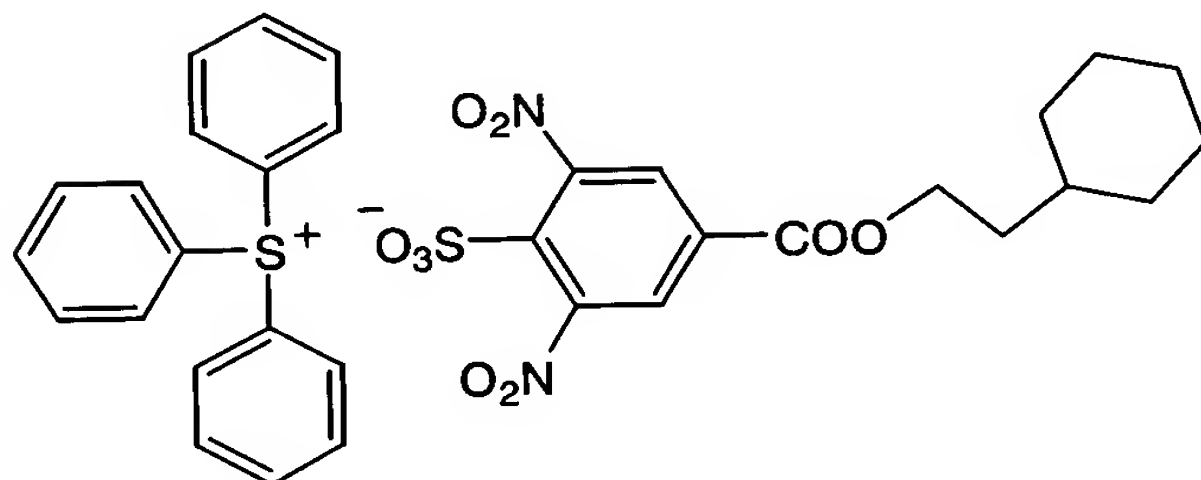
B2 :



5 B3 :

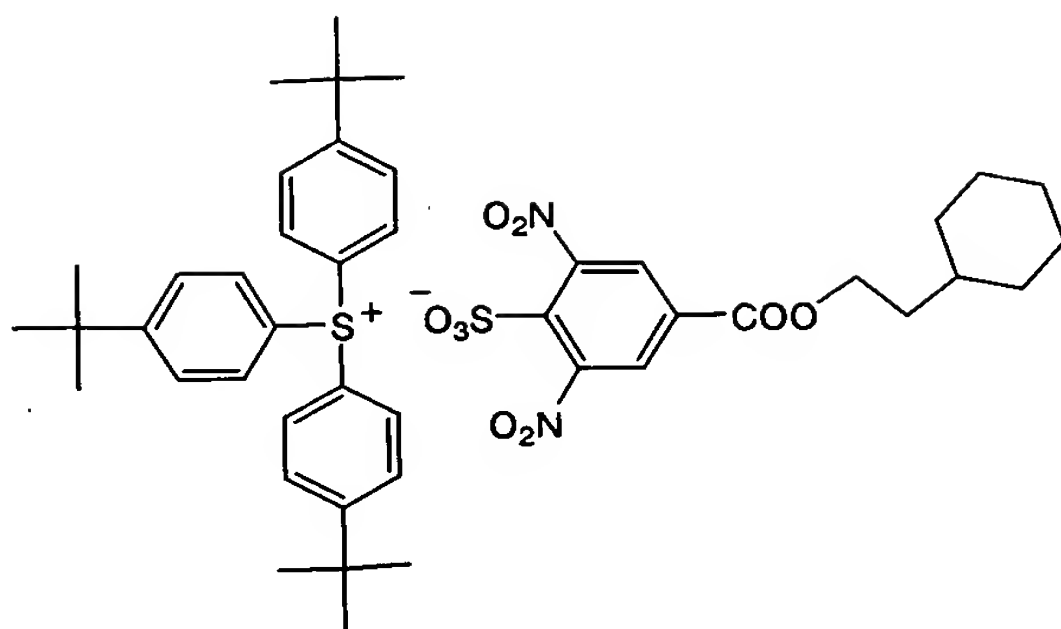


B4 :

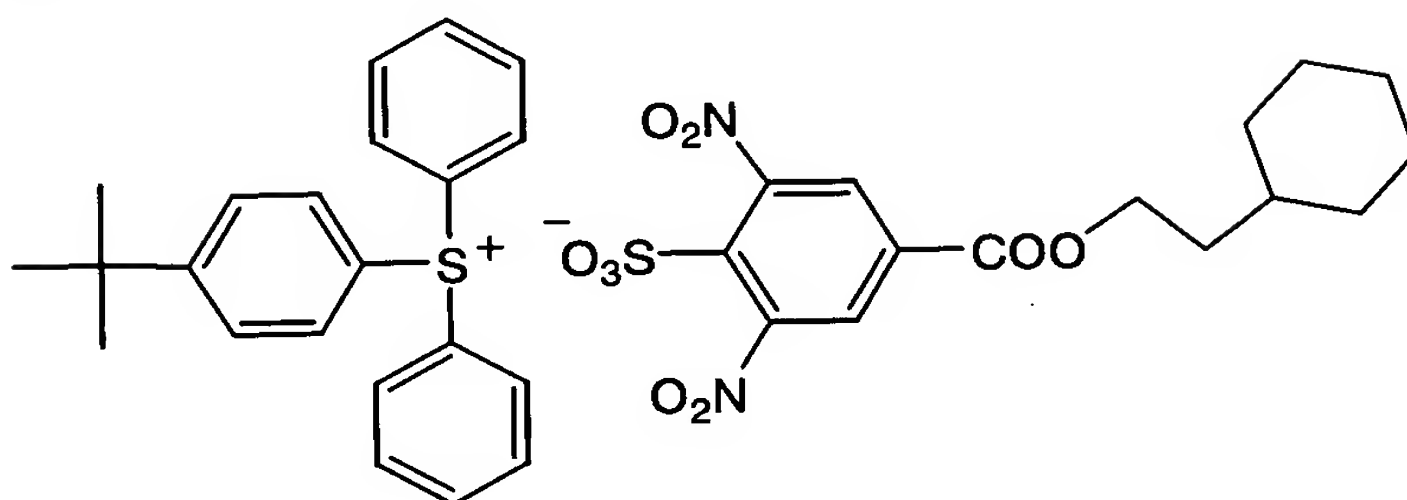


10

B5 :

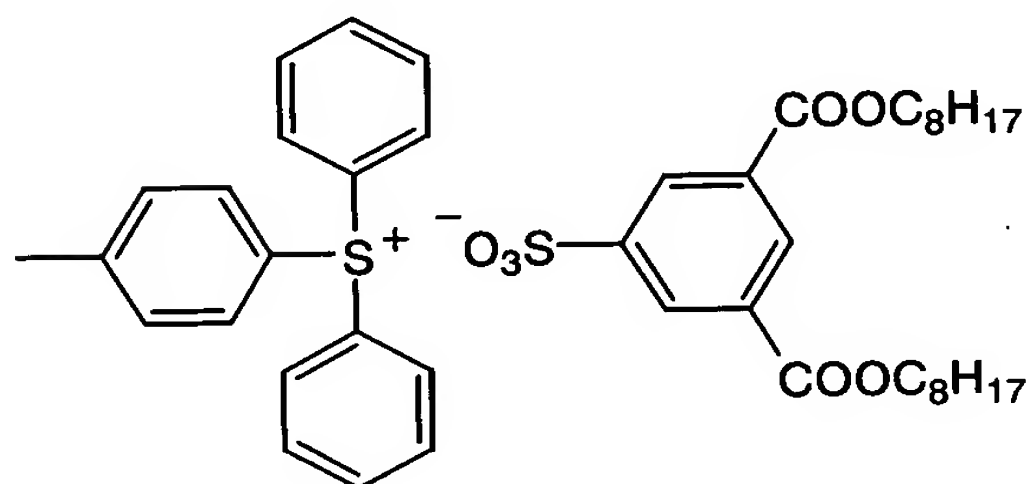


B6 :



5

C1:



<Quencher>

D1: 2,6-diisopropylaniline

10 <Solvent>

E1: propyleneglycol monomethyl ether acetate 26 parts

2-heptanone 26 parts

 γ -butyrolactone 3 parts

E2: propyleneglycol monomethyl ether acetate 57 parts

γ -butyrolactone

3 parts

[0094]

Example 1 and Comparative Example 1

The following components were mixed and dissolved, further, filtrated
5 through a fluorine resin filter having pore diameter of 0.2 μm , to prepare resist liquid.

[0095]

Resin (kind and amount are described in Table 1)

Acid generator (kind and amount are described in Table 1)

10 Quencher (kind and amount are described in Table 1)

Solvent (kind and amount are described in Table 1)

[0096]

Silicon wafers were each coated with "ARC-29A-8", which is an organic anti-reflective coating composition available from Brewer Co., and then
15 baked under the conditions: 215°C, 60 seconds, to form a 780Å-thick organic anti-reflective coating. Each of the resist liquids prepared as above was spin-coated over the anti-reflective coating so that the thickness of the resulting film became 0.30 μm or 0.25 μm after drying. The silicon wafers thus coated with the respective resist liquids were each prebaked on a direct hotplate at
20 temperature shown in "PB" column in Table 1 for 60 seconds. Using an ArF excimer stepper ("NSR ArF" manufactured by Nikon Corporation, NA=0.55, 2/3 Annular), each wafer thus formed with the respective resist film was subjected to line and space pattern exposure, with the exposure quantity being varied stepwise.

After the exposure, each wafer was subjected to post-exposure baking on a hotplate at temperature shown in “PEB” column in Table 1 for 60 seconds and then to paddle development for 60 seconds with an aqueous solution of 2.38wt% tetramethylammonium hydroxide.

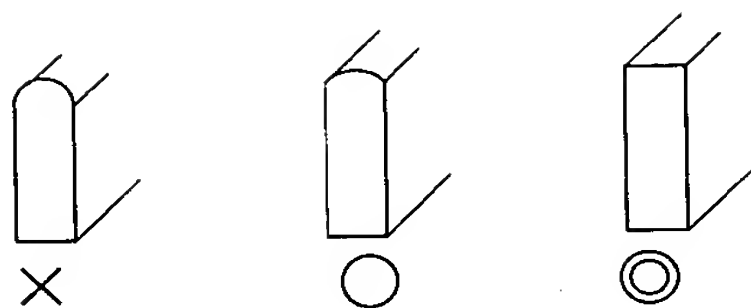
5 A bright field pattern developed on the organic anti-reflective coating substrate was observed with a scanning electron microscope, the results of which are shown in Table 2. The term “bright field pattern”, as used herein, means a pattern obtained by exposure and development through a reticle comprising an outer frame made of a chromium layer (light-shielding layer) and linear
10 chromium layers (light-shielding layers) formed on a glass surface (light-transmitting portion) extending inside the outer frame. Thus, the bright field pattern is such that, after exposure and development, resist layer surrounding the line and space pattern is removed while resist layer corresponding to the outer frame is left on the outer side of the region from
15 which the resist layer is removed.

[0097]

Effective sensitivity: It is expressed as the amount of exposure that the line and space pattern having $0.13\mu\text{m}$ become 1:1.

Resolution: It is expressed as the minimum size of line and space pattern
20 split at the exposure amount of the effective sensitivity.

Cofiguration of Resist Pattern: Cross-sectional views of resist patterns are evaluated using symbols “×”, “○” and “◎”, which represent rounded top configuration, slightly rounded top configuration and rectangular top configuration, respectively.



[0098]

[Table 1]

Example No.	Resin (Parts)	Acid generator (Part)	Quencher (Part)	Solvent	PB	PEB	Thickness of film
Example 1	A1/10	B1/0.27	D1/0.0075	E1	140°C	125°C	0.30
Example 2	A1/10	B3/0.3	D1/0.0075	E1	140°C	125°C	0.30
Example 3	A2/10	B1/0.27	D1/0.0075	E2	140°C	125°C	0.25
Example 4	A2/10	B2/0.27	D1/0.0075	E2	140°C	125°C	0.25
Example 5	A2/10	B3/0.3	D1/0.0075	E2	140°C	130°C	0.25
Example 6	A3/10	B1/0.27	D1/0.0075	E2	140°C	130°C	0.25
Example 7	A3/10	B2/0.27	D1/0.0075	E2	140°C	130°C	0.25
Example 8	A3/10	B3/0.3	D1/0.0075	E2	140°C	130°C	0.25
Example 9	A2/10	B4/0.24	D1/0.0075	E2	140°C	130°C	0.25
Example 10	A2/10	B5/0.30	D1/0.0075	E2	140°C	130°C	0.25
Example 11	A2/10	B6/0.26	D1/0.0075	E2	140°C	130°C	0.25
Comparative example 1	A1/10	C1/0.27	D1/0.0075	E1	140°C	125°C	0.30
Comparative example 2	A2/10	C1/0.27	D1/0.0075	E2	140°C	130°C	0.25
Comparative example 3	A3/10	C1/0.27	D1/0.0075	E2	140°C	130°C	0.25

5 [0099]

[Table 2]

Example No.	Effective Sensitivity (mJ/cm ²)	Resolution (μm)	Smoothness of pattern wall surface
Example 1	23	0.12	○
Example 2	30	0.12	◎
Example 3	45	0.12	○
Example 4	60	0.12	○
Example 5	75	0.12	◎
Example 6	27.5	0.12	○
Example 7	35	0.12	○
Example 8	45	0.11	◎
Example 9	27	0.12	◎
Example 10	51	0.12	○
Example 11	39	0.12	◎
Comparative example 1	18	0.12	×
Comparative example 2	33	0.12	×
Comparative example 3	21	0.12	×

[0100]

[Effects of the Invention]

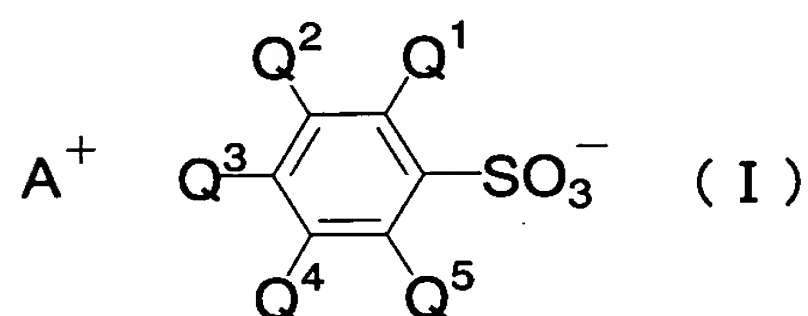
The salt of the present invention is energy-active, and can be suitably used as a component in a resist. The chemical amplification type positive resist composition of the present invention has various good resist abilities such as sensitivity, resolution, and the like, and particularly gives remarkably improved line edge roughness, and pattern profiles thereof are also good. Therefore, it is suitable for excimer laser lithography using ArF, KrF and the like, has large industrial values.

[DOCUMENT NAME] Abstract

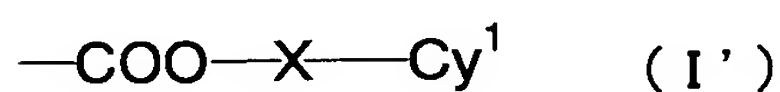
[ABSTRACT]

[PROBLEM] To provide a novel salt and to provide a chemical amplification type positive resist showing excellent various resist abilities such as sensitivity,
5 resolution and the like, and giving particularly improved line edge roughness and pattern profiles.

[SOLVING MEANS] [1] A salt of the formula (I):



wherein Q^1 , Q^2 , Q^3 , Q^4 and Q^5 each independently represent hydrogen,
10 optionally branched alkyl having 1 to 16 carbon atoms, optionally branched alkoxy having 1 to 16 carbon atoms, halogen, aryl having 6 to 12 carbon atoms, aralkyl having 7 to 12 carbon atoms, cyano, sulfide, hydroxy, nitro or a group of the formula (I')



15 wherein X represents alkylene or alkene optionally containing thioether bond or ether bond, and Cy^1 represents alicyclic hydrocarbon group having 3 to 20 carbon atoms,

and A^+ represents a counter ion, with the proviso that at least one of Q^1 , Q^2 , Q^3 , Q^4 and Q^5 is the group of the formula (I').

20 [2] A chemical amplification type positive resist composition comprising resin which has a structural unit having an acid labile group and which itself is insoluble or poorly soluble in an alkali aqueous solution but becomes soluble in

an alkali aqueous solution by the action of an acid, and a salt described in [1].

[SELECTED DRAWING] None